NOVEL INTEGRITY MONITORING TECHNIQUES FOR HIGH-PRESSURE

MEMBRANES (NANOFILTRATION AND REVERSE OSMOSIS)

by

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ABSTRACT

High-pressure membrane processes such as nanofiltration (NF) and reverse osmosis (RO) are becoming more common in water treatment trains designed to produce high quality effluent from impaired water resources (e.g., potable reuse; desalination) due to their ability to remove dissolved contaminants, salinity, and harmful pathogens. Various drinking water regulations require that water treatment systems achieve at least 4-log removal of pertinent pathogens, dependent on the source water, through a combination of treatment approaches. While previous studies investigating high pressure membrane treatments have demonstrated greater than 5.0-log removal of these pathogens (99.999% removal), only 1- to 2-log pathogen removal credits are granted due to limitations in accepted membrane integrity monitoring techniques. A thorough review of the substantial work that has been dedicated to improving the log removal values granted to high pressure membrane systems revealed that while there are integrity monitoring methods that are able to achieve log removal values above 3-log, only a small subset can be realistically applied by facilities employing high-pressure membranes. From this small subset, two potentially viable integrity monitoring methods were chosen for further investigation. The first method evaluated the calculation of log removal values for full scale membrane systems using statistical analysis of conductivity profiles. The second method evaluated the application of the promising chemical markers identified in a literature review on a closed circuit system. The statistical analysis of conductivity profiling data from two separate facilities resulted in calculated log removal values greater than 3-log, as opposed to values of only 1.5- to 2-log obtained using combined permeate calculations. Sampling and analysis of strontium and two fluorescent dyes during operation of a closed circuit desalination system was able to demonstrate removals of 3.25-log and 2.5-log, respectively. The use of statistical analysis and strontium monitoring both have the ability to demonstrate higher removal capacity of intact membranes than current methods without adding undue cost to the facilities that implement them.

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CHAPTER 1

INTRODUCTION

High-pressure membranes, including reverse osmosis (RO) and nanofiltration (NF), are widely used in water treatment (e.g., groundwater, surface water, seawater) and reuse (indirect and direct potable reuse) applications. High-pressure membranes are often utilized in a treatment system because they are highly capable of rejecting dissolved ions in water and produce exceptionally clean treated water. Multiple state and federal regulations have been put into place regarding these water treatment systems with the goal of protecting human health. These regulations require the regular monitoring of a treatment technology to ensure there are no defects that would allow the passage of pathogens such as viruses, *Cryptosporidium*, and *Giardia* into the treated water through the calculation of a log removal value (LRV). While the United States Environmental Protection Agency has passed regulations for drinking water treatment that requires 4-log removal of viruses, indirect and direct potable reuse regulations are much more protective of human health and require the demonstration of more than 12-log removal of viruses for a water treatment system with a maximum of 6-log for an individual technology.

In theory, this makes high-pressure membranes an ideal treatment technology, as they serve as a considerable barrier to pathogens and have demonstrated removals above 5-log on intact membranes. However, regular demonstration of the removal capacity and monitoring of RO and NF membranes has proven difficult due to a combination of factors. High-pressure membranes are typically one of the final steps in a treatment process, and the water that is used as their feed has already been treated by a variety of other technologies so feed water already has very low concentrations of viable markers. Naturally occurring markers that have been accepted by regulators are limited to removal values of 2-log or lower, substantially below the true removal capacity of high pressure membranes. The addition of surrogate markers has been explored, but these markers are typically expensive to administer or require costly and time consuming analysis. Additionally, many of these markers are smaller than the viruses they are serving as surrogates for and able to diffuse through the membrane and into the permeate. These potential markers are limited to conservative estimates of membrane integrity, and typically receive similar log removal credits to the currently accepted methods of integrity monitoring. In addition, while specific methods for the integrity monitoring of membranes have been specified as part of the Membrane Filtration Guidance Manual (MFGM), these methods better fit the operation of low-pressure membranes (i.e., ultrafiltration and microfiltration) and provide minimal insight into the unique aspects of high-pressure membranes.

The disparity between the true removal capacity of an intact high-pressure membrane system and the log removal credits such systems are currently able to receive is a substantial hindrance to the wider use of high pressure membrane systems. The identification of an integrity monitoring method that is both

able to demonstrate log removal values above 3-log while remaining a practical and realistic option for facilities utilizing high-pressure membranes was the goal of this research and led to the development of several objectives.

The first objective was to complete a thorough literature review to understand the current state of research on integrity monitoring of high pressure membranes and identify promising monitoring methods for further evaluation. Although a substantial amount of research has been completed on high pressure membrane monitoring, there has been minimal change in integrity monitoring methods used at full scale facilities. The MFGM was thoroughly reviewed and used as a guide to evaluate the methods of integrity monitoring identified in the literature review. This literature review was used as a guide to select several novel and practical monitoring methods for further evaluation, including whether or not the approaches could fit within the regulations set forth by the MFGM and state regulators. This in depth literature review can be found in Chapter 2.

Of the methods identified in the literature review, statistical analysis of conductivity profiles showed great promise as an integrity monitoring method. This method, proposed by Jim Vickers [1], is only just beginning to be explored. The establishment of associated statistical rules and limits can reportedly improve the log removal credits obtained for a high pressure membrane system and standardizes the identification of pressure vessels where defects are potentially located. The statistical approach has only been implemented at a limited number of facilities and further evaluation is needed in order to demonstrate its reliability and accuracy. The statistical method was used to analyze conductivity profiling data from two full scale RO systems that provided data as part of a partnership with a Water Research Federation project. A discussion of the statistical rules and limits proposed by Vickers can be found in Chapter 3, and the results of the facility analyses can be found in Chapter 4.

The literature review also identified several chemical markers whose monitoring may result in quantifications of removal values greater than 2-log. Of these markers, strontium and two fluorescent dyes (uranine and rhodamine B) were chosen for further investigation using a closed-circuit desalination (CCD) system. The recirculation aspect of the CCD system allowed for the calculation of log removal values at progressively higher feed concentrations, as the concentrate was mixed with influent at a steady rate, and a theoretical maximum log removal value could be calculated. A description of the CCD system, as well as the markers evaluated, can be found in Chapter 3 and the experimental results can be found in Chapter 4.

No review of integrity monitoring methods would be complete without discussing their real world applicability. Many of the methods reviewed in the literature review and discussed in Chapter 2 have been demonstrated and tested on pilot scale systems, with little thought to their application on full scale

systems. As such, the final goal of this research was to consider just that aspect of integrity monitoring. A final takeaway for this research can be found at the conclusion of this paper, Chapter 5.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Traditionally used as a key component in desalination processes, intact RO and NF membranes are capable of highly rejecting dissolved ions in water, and therefore sufficient to act as a substantial barrier to pathogens such as virus, *Cryptosporidium*, and *Giardia*. The control of waterborne pathogens is of paramount importance to the protection of human health, and thus is the focus of several regulations that impact treatment systems employing RO/NF, including:

- California Code of Regulations (Title 22) Groundwater Replenishment and Surface Water Augmentation Regulations – Requires at a minimum, 12-log virus, 10-log *Giardia* and 10-log *Cryptosporidium* removal by reclaimed water systems used for indirect potable reuse (IPR). Each treatment process can be given up to 6-log removal credit, and at least four treatment technologies are required [2].
- United States Environmental Protection Agency (USEPA) Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) – Requires 4-log removal of enteric viruses, 3-log *Giardia* and up to 5.5-log *Cryptosporidium* removal by drinking water treatment systems depending on source water quality [3].
- USEPA Groundwater Rule – Requires 4-log removal of enteric viruses for groundwater sources determined susceptible to fecal contamination [4].

Currently, California and other U.S. states, i.e., Texas, New Mexico, and Arizona have or are working on direct potable reuse regulations and/or guidelines with similarly high pathogen log removal value (LRV) requirements. Because of the acute public health implications associated with pathogens, drinking water regulations require performing both continuous indirect integrity monitoring (CIIM) and a once-daily direct integrity test (DIT) for membrane treatment systems. Based on the USEPA's Membrane Filtration Guidance Manual (MFGM) [5], which was developed for use in conjunction with implementation of the LT2ESWTR for *Cryptosporidium* removal, a DIT must have the resolution (i.e., size) and sensitivity (i.e., amount removed) to quantify the log-removal credit sought for virus, *Cryptosporidium*, and/or *Giardia*.

Based on the size of pathogens and the molecular weight cutoff values for RO and NF membranes (Figure 2-1), high-pressure membranes should easily achieve high log-removal credits for virus and protozoa as defined by the regulations summarized above [5]. Meeting the integrity monitoring requirements specified in the MFGM and demonstrating more than 2-log removal, however, has proven a challenge. One difficulty has been identifying native markers or surrogates that have the resolution and

sensitivity necessary in a high-pressure membrane system's feed and permeate for demonstrating an LRV value greater than 3-log due to a variety of reasons (e.g., analytical measurement limitations, cost, lower than ideal rejection, non-detects in the permeate, etc.). Additionally, some DIT requirements (e.g., California) specify that subsets or individual vessels of membrane systems must be tested for continuous indirect and once-daily direct testing, necessitating the development of an easy-to-implement approach. Finally, high-pressure membrane systems can be compromised through a variety of mechanisms; a survey completed by Jacangelo et al. [6, 7] reported that damaged O-rings, glue line leaks, and particulate damage accounted for the majority of breaches. These breaches may be sufficient to allow pathogens to pass through the membrane and into the permeate.

Figure 2-1: Filtration Application Guide for Pathogen Removal [5]

According to Vickers et al. [8], LRVs of 1.5 for viruses, *Giardia*, and *Cryptosporidium* are appropriate as a result of the lack of a DIT methodology for RO and NF systems in spite of MS2 bacteriophage, a MFGM approved virus surrogate, removals of greater than 6-log at the bench scale [9-13] and greater than 5-log through a full-scale system at the Yucaipa Valley Water District [8]. The absence of a validated DIT method with the resolution and sensitivity required to quantify greater than 1.5-log and at least 4-log removal in high-pressure membrane systems is not due to a lack of effort. Easily measured bulk chemical surrogates (e.g., organic carbon and conductivity) typically demonstrate less than 2-log removal and lack the MFGM's requirements for resolution to be directly attributed to the size of virus or pathogen required for a DIT. Select chemical constituents are also not typically present at concentrations in feed water that meet the MFGM's requirements for sensitivity to quantify 4-log removal [8-10].

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Findings from past research on NF and RO membranes indicate that identifying indigenous molecular markers that can meet the USEPA MFGM's requirements for resolution and sensitivity in a DIT method to demonstrate removal of 4-logs or higher is challenging. As an example, log-removal of various constituents by a full-scale RO membrane treatment train at the Orange County Water District's Water Replenishment System is presented in Figure 2-2. Of the inorganic and organic solutes detected in feed and permeate streams of the full-scale membrane system (>30 constituents total), only magnesium, sulfamethoxazole, gemfibrozil, and naproxen can be used to demonstrate greater than 3-log removal. Furthermore, without isolating the difference between "defects" versus "diffusion" of these constituents, which is permitted by the USEPA MFGM, none of the identified parameters yielded greater than 4-log removal. However, it should be noted that native DOC and UV_{254} do not meet the USEPA MFGM's requirements for a DIT's sensitivity since the size of these parameters are not uniform and therefore not comparable to the size of virus or pathogens.

Figure 2-2: Log-removal of several surrogates and indicator compounds by a full-scale membrane system at the Orange County Water District Groundwater Replenishment System [14]

This literature review summarizes the previous studies and research pertaining to integrity testing regulatory framework and development of approaches for ensuring membrane system integrity and ultimately claiming LRV for high-pressure membrane systems greater than 2-logs and ideally equal to or greater than 4-logs. It is worth noting that several reviews on high-pressure membrane integrity have

recently been published [7, 10, 15, 16]. In particular, Jacangelo et al. [7] recently conducted a literature review that provided a comprehensive list of high-pressure membrane integrity approaches.

2.2 Integrity Testing Regulatory Framework

The Long Term 2 Enhanced Surface Water Treatment Rule (LT2ESWTR) was introduced in 2006 to provide additional requirements for drinking water systems to control *Cryptosporidium* and other pathogens in surface water sources [5]. As part of the LT2ESWTR, the EPA released the MFGM to provide guidance for regulators and municipalities to understand how membrane technologies fit into the LT2ESWTR framework, as well as establishing guidance regarding their use and implementation. The MFGM also established means of communicating the removal efficiencies of membranes through the log removal value (LRV). LRVs are established using Eqn. 2.1:

$$LRV = \log(C_f) - \log(C_p) \tag{2.1}$$

where, LRV is the log removal value demonstrated during testing, C_f is the measured feed concentration, and C_p is the measured filtrate (for MF/UF) or permeate (for RO/NF) concentration.

The LRV that a membrane receives is the lower of two demonstrated values: (1) the removal efficiency demonstrated during challenge testing or (2) the maximum LRV that can be verified by a DIT used during the course of normal operation. Challenge testing was established to be product specific and is typically performed a single time by the membrane manufacturer in accordance with NSF/ANSI 419. Membrane manufacturers typically sponsor challenge testing of their products, which is typically performed by a qualified third party such as NSF. DITs, on the other hand, must be applied to all physical elements of the entire membrane units, including all non-membrane components that could result in the contamination of the filtrate (i.e., membrane permeate) if compromised, on a frequency of once per day. Additionally, a membrane unit must have a method for continuous indirect integrity monitoring (CIIM) which involves the monitoring of some aspect of the permeate water quality. The chosen water quality aspect serves as a surrogate to membrane integrity, as changes in permeate quality can indicate a compromise in membrane integrity [5]. Membrane manufacturers typically sponsor challenge testing of their products, which is typically performed by a qualified third party. It is worth noting that the MFGM does not explicitly define acceptable DIT and CIIM approaches for high-pressure membranes (RO and NF), and as a result, there is some ambiguity regarding whether a specific method constitutes a DIT versus a CIIM approach. The following sections define DITs and CIIMs in accordance with the MFGM. Additionally, many of the requirements set forth by the MFGM focus on MF and UF membranes as opposed to RO and NF membranes. The following discussions consider the challenges in applying these methods to high-pressure membrane systems.

2.2.1 Direct Integrity Testing

Direct Integrity Testing (DIT) is defined by the LT2ESWTR as a physical test applied to a membrane unit in order to identify and isolate integrity breaches. DIT is required to be completed on every membrane actively used at a frequency of at least once per day, except if State approval has been given for less frequent testing based on demonstrated process reliability, the use of multiple barriers against *Cryptosporidium*, or reliable process safeguards. The test must have the resolution to detect an integrity breach relating to the removal credit given. This corresponds to less than 3 μm for *Cryptosporidium* and *Giardia,* and less than 0.01 μm for viruses. The test must also have the sensitivity to verify an LRV greater than or equal to the removal credit awarded to the entire membrane filtration process.

2.2.1.1 Pressure Based Testing

One of the most common DIT methods is pressure decay testing or vacuum decay testing. The MFGM allows pressure-based direct integrity testing based upon a calculation of air flow through an orifice, the size of which can be equated to the pathogen size for which removal is sought (e.g., 3 μm). Air flow is equated to air pressure decay in these tests, and allowances for air diffusion through the intact membrane are also considered and incorporated into the test method. This allows isolation of "diffusion" related air pressure decay from the "defect" related pressure decay. These tests are common for their relatively low cost and acceptance by State and Federal regulators. However, the tests must be done offline and do not have the sensitivity required to detect virus-sized defects without causing damage to the membrane element. According to Table E.4 of the MFGM [5] the required test pressure to target virus sized pathogens, the smallest of which are 0.01 μm, would range from 768 to 4,344 psi. This exceeds the pressure that a typical commercially available membrane system can withstand without damage [5]. Pressure based testing is applicable for the detection of mechanical integrity problems, however it cannot be performed online and often requires the units to be drained, which can result in damage to or fouling of the membrane elements [17]. While pressure decay testing is a standard practice for the MF/UF industry, it has logistical challenges that make it difficult to implement on full-scale RO and NF systems. Specifically, the system must be drained in order for the results to be reproducible and the orifice (pressure or vacuum decay) calculation to work. Horizontally oriented RO and NF systems cannot drain completely, rendering the test inapplicable to NF/RO membranes.

2.2.1.2 Marker-Based Testing

The second type of DIT presented in the MFGM is a marker-based test. In this test, a surrogate is periodically applied to the feed water in order to verify the membrane system integrity. In order to qualify for virus LRVs, the surrogate must be in the size range of 0.03 to 0.1 μm (i.e., resolution). An approved

surrogate for viruses in the MFGM is the male-specific coliphage (MS2), with a size of 0.01 μm [5]. In addition to being a similar size, MS2 bacteriophage also has a similar shape and composition to viruses, making it an attractive substitute [17]. The use of MS2 bacteriophage has been widely studied, and LRVs of greater than five are typically achieved across intact membranes, with some reports of greater than seven [10, 17, 18]. Despite its wide use, the use of MS2 bacteriophage is not without its drawbacks. Production of a sufficient amount of MS2 for a full-scale facility is time-consuming and logistically challenging. False positives have also been reported [19], and time-consuming testing must be done at a specialized laboratory. Additionally, there are concerns regarding the release of the large concentrations of MS2 necessary for full-scale DIT [18]. For these reasons MS2 testing is more often used for challenge testing purposes to compare other surrogates against, as opposed to daily integrity testing. However, the LT2ESWTR does not require the use of a particular DIT for rule compliance, but rather that any test used must meet the specified performance criteria for resolution, sensitivity, and frequency [5]. Therefore, a sizable amount of research has been undertaken to identify surrogate markers (e.g., molecular markers) that meet the requirements of the MFGM and result in appropriate LRV credits. These alternate surrogates are discussed in more detail herein.

2.2.1.3 Dilution or Imperfection LRV Calculations

Recently, several approaches have been developed to improve LRVs calculated from DIT and CIIM monitoring data. This concept is analogous to pressure decay test data evaluation where the rate of diffusion of air through an intact membrane is subtracted from measured air diffusion rates during DIT measurements (i.e., dilution approach, MFGM Section 4.3.1.3) [5]. In a similar approach, Vickers [1] used statistical analysis of conductivity profiling data to calculate the permeate conductivity due to diffusion and the permeate conductivity due to a defect for LRV calculations. More information on this approach is provided in Section 2.3.2.4, but studies have demonstrated LRVs greater than 3 using this approach [1, 20].

Other researchers [15, 21, 22] have applied the solution-diffusion-imperfection model as an approach for high-pressure membrane system DIT. Because RO and NF membranes do not have pores, salt removal is controlled by diffusion. The rate of diffusion can be calculated based upon the mineral composition in the feed water and temperature. Accounting for the water flux through the membrane, the concentration of easy-to-measure constituents in RO or NF permeate water can be calculated. If the measured concentration matches or is less than the calculated value, integrity can be demonstrated in a manner equivalent to that used for a pressure based DIT. With this methodology, the model is calibrated to intact membrane specimens and applied to permeate water quality obtained semi-continuously along with membrane system operating parameters. From this approach, solute specific model parameters (e.g., solute permeability, solute leakage factor) can be calculated and compared to values obtained from intact

membrane specimens with deviations indicating an integrity issue. While several studies have demonstrated the effectiveness of this approach [15, 21], actual LRVs that could be obtained from this method have not yet been firmly established and regulatory approval has not yet been requested. This approach would likely require membrane system profiling to meet the requirements of a DIT per the requirements of the MFGM.

2.2.2 Continuous Indirect Integrity Monitoring

In the MFGM, continuous indirect integrity monitoring (CIIM) is defined as "monitoring some aspect of filtrate water quality as a surrogate measure of membrane integrity" [5]; though this definition focuses on low-pressure membrane monitoring, as indicated by the use of the filtrate term. Although the methodology of CIIM does not need the same level of sensitivity and resolution constraints that a DIT method does, a marked decline in filtrate quality can serve as an indicator for membrane integrity problems. While low-pressure membrane filtrate quality is very consistent and is largely independent of fluctuations in feed water quality, the same is not true for high-pressure membranes. While fluctuations in a chosen parameter would be indicative of an integrity breach in a UF/MF membrane system, the same response to a defect cannot be guaranteed for a RO/NF membrane. CIIM must be separately conducted on each membrane unit at a frequency of at least once every fifteen minutes. While LT2ESWTR and the MFGM don't specify any criteria for resolution and sensitivity relating to CIIM, they do require the establishment of performance-based control limits. If readings fall outside these control limits for a period of longer than fifteen minutes (two consecutive readings), a DIT must be done to assess a potential integrity problem. It should be noted that while CIIM is currently the standard, the MFGM has acknowledged that the development of a sufficiently sensitive and reliable continuous DIT is feasible, and a proven test of this caliber could preclude CIIM at a federal level, State requirements notwithstanding [5].

2.2.2.1 Turbidity

The MFGM states that unless there is a State-approved alternative parameter in use, filtrate turbidity monitoring must be implemented. Turbidity monitoring has well-defined control limits, with consecutive readings above 0.15 NTU indicating a loss in integrity and requiring direct integrity testing in MF/UF membranes. Despite these well-defined parameters, it has a low sensitivity to breaches that would allow the passage of virus particles [5]. Even laser turbidimetry, capable of measuring much lower turbidity values than traditional turbidimeters, is limited to particles over 1000 nm, ten times larger than even the largest virus particle [17]. Additionally, while laser turbidity has been shown to be able to detect a single broken fiber on a UF membrane module with several thousand fibers (pore size ~0.1 microns), it is unclear how well this would apply to higher pressure membranes like RO or NF [23]. In practice, the

use of turbidity, even at the detection level allowed by laser turbidimetry, would be unlikely to work for high-pressure membranes, as feed waters typically undergo pre-treatment though MF/UF that substantially reduce the number of particles that can be detected [24].

2.3 Molecular Markers for DIT

2.3.1 Fluorescent Dyes as Markers for Membrane Integrity

Fluorescent dyes are common tracers in water studies, having been used to study flow, mixing, and other properties of natural and man-made water systems. Fluorescent molecules work by absorbing light of a certain frequency, then emitting light at a different frequency. In order to be used as a tracer, a fluorescent molecule or dye must be able to emit at a frequency that will be unique from other fluorescing compounds potentially in the water source. The molecule must be stable under a wide variety of conditions, and not be altered by exposure to oxidizers, acids, bases, sunlight, microorganisms, or changes in pH, conductivity, hardness or temperature. Additionally, the molecule must remain in the water, and not be removed by corrosion byproducts or precipitate out of solution [25]. All of the fluorescent dyes considered for use as a molecular marker DIT surrogate are significantly smaller than virus particles, meaning they provide conservative estimates of membrane integrity. Dyes with larger molecular weight would theoretically yield higher calculated rejection values (i.e., LRVs), and be able to provide more accurate estimates of virus rejection, giving a more accurate representations of membrane integrity. Due to the sensitivity of fluorophore analysis and availability of online fluorescent analyzers, it may be possible to apply either: (1) a dilution model approach similar to that described in the MFGM for pressure-based testing (i.e., using air) and by Vickers using conductivity [1], or (2) the imperfection model approach described by Frenkel and Cohen [21] using an organic fluorophore. Such approaches would require instrumentation to conduct fluorescence profiling on a high-pressure membrane system (e.g., RO system), but could potentially yield higher LRVs by accounting for diffusion and separating this from defect caused fluorescence.

2.3.1.1 Uranine

A number of studies have been performed evaluating the use of fluorophores for monitoring membrane integrity [7, 16, 21, 26]. Of the four fluorescent dye candidates (eosin, fluorescein, rhodamine-WT, uranine) selected by Frenkel and Cohen [21] from a larger list of commercially available dyes (Table 2-1), uranine was selected for further testing due to its high sensitivity. Membrane filtration evaluations using uranine as a marker with the Hydranautics ESPA2 membrane demonstrated LRV calculations between 3.8- and 4.4-log at a nominal feed concentration of 40 mg/L depending on permeate flux. Subsequent evaluation of intentional integrity breaches (i.e., pin holes, membrane degradation due to oxidation) demonstrated that uranine fluorescent monitoring was sensitive enough to detect relatively

small breaches [21]. These results are comparative to results gathered by Jacangelo and Gray [6], where uranine demonstrated average LRV calculations of 3.96-log with a continuous feed concentration of 1 mg/L. The comparative LRV calculations for the different feed concentrations suggest that lower feed concentrations may be possible while maintaining sufficiently high LRV [6].

In addition to identifying of viable fluorescent markers for integrity monitoring, Frenkel and Cohen [21] developed a testing approach termed pulsed-marker membrane integrity monitoring (PM-MIMo) using uranine as the fluorophore. The PM-MIMo approach monitors the permeate fluorescence of a pulsed mass of uranine into the membrane feed water (although it could be any fluorescent marker) to determine the fraction of mass breaching the membrane in a specified time period. This mass fraction is continuously compared with experimentally determined mass fraction values of an 'intact' membrane to determine if integrity has been breached. Conceptually, this approach is similar to that of Vickers et al. [1, 8, 20] (i.e., dilution model for conductivity) and could theoretically be used with any molecular marker. In addition, the researchers evaluated the use of the Spiegler-Kedem (or phenomenological) model to distinguish between diffusive and convective transport [21].

Table 2-1: Various fluorescent markers evaluated in WRF-09-06b for inclusion in membrane integrity testing.

Fluorescent Marker	Excitation/Emission Wavelength (nm)	Molecular Weight (g/mole)	Aqueous Solubility (g/L)
Rhodamine-WT	554/580	480.55	
Rhodamine-B	554/576	479.02	50
Rhodamine-6G	526/552	497.02	20
Sulforhodamine-B	554/576	580.65	10
Amidorhodamine-G	530/551	552.59	Very Soluble
Fluorescein	490/520	332.31	0.3
Uranine	491/512	376.28	40
Eosin-B	516/538	691.88	40
Pyranine	455/512	524.39	178
Tinopal CBS-X	346/435	526.57	25
Erythrosine	525/547	879.87	20
Sodium naphtionate	320/430	245.23	240
Lanaperl fast yellow	469/508	549.55	Very soluble
Lissamine-FF	432/508	404.38	40
Bengal Rose	518/535	1017.67	100
Fluorescent brightener	349/430	960.96	Very soluble

2.3.1.2 3D TRASAR ®

Nalco Water, an Ecolab company, originally developed 3D TRASAR (Trasar) as a monitoring additive for cooling towers and other water circulation systems, but it has also shown promise as a molecular tracer to monitor the integrity of high-pressure membranes [27]. Trasar is a purportedly discontinued Nalco product that contains an organic fluorophore that can be tracked through fluorescence measurements in near real-time [12]. The addition of Trasar results in fluorescence at a level that is distinct and easily correlated to a concentration of the molecular tracer in the membrane feed and permeate water while being easily distinguished from natural fluorescent particles that may be present [28]. The molecule can be detected at a concentration as low as 10 μg/L with an online sensor [12]. The molecule is considered chemically inert and is blended with other select Nalco products (e.g., antiscalant, biocide) [25]. When used for high-pressure membrane monitoring, it is typically combined with an antiscalant, though studies have shown improved LRV's without the antiscalant [17, 18, 29]. Trasar is considered a conservative measure of membrane integrity, as the fluorophore has a molecular weight of 614 g/mol, much smaller than virus particles (20,000 to 200,000 g/mol). The molecule is also negatively charged, which can help mimic the charge repulsion experienced by similarly charged virus particles, but also increases rejection across the system [12]. Trasar fluorescence also has the advantage of not requiring reagents, and measurements are relatively simple and rapid to obtain, typically with immediate results [25].

During operation, the Trasar dye is added as a continuous dose to the feed water and the fluorescence output is monitored with an online sensor, which is correlated to the mass concentration of the molecular tracer in the water through standard calibration methods. A raw water production facility in Big Spring, Texas was able to collect readings as often as once per minute as part of their investigation into Trasar technology; fluorescence data collection on such a rapid scale led to an immediate identification of an introduced cut O-ring, reducing the chance of virus passage and risk to human health [12]. This facility measured LRVs of 4.3-log across intact membranes and saw lowered removals in the second stage due to fouling from long-term use prior to experimentation [12]. Similar LRVs were seen during other studies, with typical values between 4- and 4.5-log when Trasar was added with the antiscalant [6, 9, 18], but with values as low as 2-log also reported [17]. However when uncoupled from antiscalant addition, Trasar was able to provide LRVs of greater than 6-log, providing some evidence the exclusion of antiscalant may provide better information on membrane integrity [17, 30]. Jacangelo and Gray [6] also saw an increase in recorded LRVs when Trasar was added as a pulse instead of a continuous dose. Pulsing Trasar into the system also allowed for higher concentrations to be used without incurring

additional costs or risk of membrane fouling. In this study, the researchers found that calculated LRVs increased with pulsed Trasar addition from 4.59- to 4.91-log [6, 7].

While Trasar does provide a conservative estimate of membrane integrity due to the size of the fluorophore relative to a pathogen, evidence has shown that the effect of aging and oxidation disproportionately affects Trasar removals as compared to MS2. The integrity study conducted at Big Spring showed that intentionally oxidized membranes had an LRV reduction to 3.6-log for Trasar (compared to 4.3-log before oxidation occurred), while MS2 removal reportedly remained steady [12]. Oxidation damage and aging effects therefore appear to be conservatively captured by Trasar before integrity breaches negatively impact the actual LRVs of pathogens. Therefore, while the USEPA MFGM requires that a DIT must be sensitive enough to determine if particles the size of virus are removed, if an increased concentration of a molecular tracer in the membrane permeate is uniformly distributed across a membrane train as a result of oxidation and aging damage, the uniformity of this concentration can be attributed to increased diffusion as opposed to a defect, and if a challenge test demonstrates sufficient LRV, the challenge test LRV credit can still be used for compliance. The acceptable concentration of a molecular tracer in membrane permeate under this oxidized or aged condition should be included as a boundary limit within the challenge testing protocol, meaning that a maximum molecular tracer concentration in the membrane permeate should be attributed to an acceptable challenge test LRV for MS2 phage.

2.3.1.3 Rhodamine WT

Rhodamine WT (R-WT) is another potential fluorescent molecular tracer for use in integrity monitoring. R-WT is a non-reactive tracer chemical that has been approved by the USEPA for use in drinking water systems. It was specifically formulated for water tracing applications, both natural and man-made [31, 32]. R-WT has a molecular weight of 487 g/mol, smaller than TRASAR, and is negatively charged at pH typical of RO and NF membrane feed water (i.e., pH 6 to 7). R-WT is expected to be rejected in a membrane system via charge repulsion and size exclusion and can be detected in the ng/L range [33, 34]. These aspects combined with its stability under a wide range of environmental conditions [35, 36] make R-WT a promising molecular tracer to be used for membrane integrity monitoring and as such it has been widely studied. A summary of these studies and their removal values are shown in Table 2-2 below. Feed concentrations have been included for reference, as evidence shows that higher feed concentrations result in high LRVs. However, there is evidence that higher concentrations of dye in the feed can lead to adsorption and increase the risk of membrane fouling [37].

Table 2-2: Summary of Rhodamine WT studies

Feed Concentration (mg/L)	Dosing mode	LRV	Reference
0.1 – 1.0	Continuous	3.5 – 5.3	[33]
1.0 – 2.0	Continuous	3.9	[34]
1.0	Continuous	2.7 – 3.0	[10]
0.1 – 1.0	Continuous	2.0 – 5.0	[26]
0.1	Continuous	2.6	[38]
1.0	Continuous	4.19	[6]
5.0	Pulsed	4.77	[6]
5.0 – 10.0	Pulsed	>4	[29]

2.3.2 Conductivity Monitoring

2.3.2.1 Introduction

A common alternative to turbidity measurements (discussed in section 2.2.2.1) used in high-pressure membrane applications for both DITs and CIIM is electrical conductivity monitoring. Conductivity is considered a surrogate for total dissolved solids (TDS), and conductivity monitoring is relatively easy to implement because conductivity instruments are relatively inexpensive, stable, reliable, and require limited maintenance. In 2015, Jacangelo and Gray [6] conducted a survey on five utilities utilizing RO membranes as part of their treatment process. Of these facilities, all five had conductivity monitoring in place as an RO permeate monitoring technique, although conductivity measurements were not being used to monitor membrane integrity and instead focused on plant performance. Conductivity monitoring is also an accepted method of integrity monitoring because of the relative confidence regulators have in TDS rejection; dissolved solids and ions are of a size that is substantially smaller than known virus or protozoa. Sodium chloride, for example, has a Van der Waals radius of 0.282 nm, several orders of magnitude smaller than even the smallest known virus [18]. Conductivity monitoring is further supported as a measure of membrane integrity because RO membranes are highly efficient at removing salts. Feed waters tend to have high ambient levels of salts that additional seeding is not required to achieve removals up to 2-log. Conductivity measurements are a common method of integrity monitoring despite the relatively low LRV credits that are currently awarded, but there has been little research in the past that has focused on the process. It is not uncommon to see conductivity results reported in past research, but they are often reported as comparisons for surrogates or alternative methods. A summary of conductivity LRV's reported as part of other research projects can be found in Table 2-3. Conductivity

measurements can be collected either continuously online or through periodic profiling (i.e., testing of each pressure vessel in a membrane train), with both methods having benefits and drawbacks.

Table 2-3: Observed LRVs using conductivity in various studies

Observed LRV	Facility Information	Main Integrity Test	Reference
1.7	Big Spring, Texas 2-Stage Pilot Scale	Trasar	[9]
2.43	Kamerik, Netherlands Parallel 8" RO elements Recirculated water Temperature controlled	Natural Viruses	[13]
1.7 – 1.8	Gippsland Water Factory	R-WT	[39]
1.5	Fountain Valley, California 5 MGD 3-Stage	Naturally occurring surrogates	[40]
~1.5	Big Spring, Texas 2.38 MGD 2-Stage	Trasar	[12]

2.3.2.2 Continuous Online Conductivity Analysis on Combined Permeate Streams

Continuous online conductivity measurements provides a real-time evaluation of a system's gross integrity, as online conductivity has been shown to be sensitive enough to detect major breaches in a system (i.e. damaged O-rings) [24]. As stated in Section 2.3.2.1, conductivity measurements are widely accepted as a surrogate for TDS and have been historically accepted as a method of continuous and direct integrity monitoring. However, the resolution of this method may vary depending on the size of a train and the number of pressure vessels contributing permeate water to the online instrument. As shown in Figure 2-3 below, which shows an example of a typical three-stage RO unit, conductivity analyzers are typically installed at locations where waters from multiple vessels have already combined.

Figure 2-3: Typical three-stage reverse osmosis unit instrumentation [1]

Permeate conductivity measurement can be affected by changes in temperature, feed TDS composition and/or concentration, pressure, flux, fouling, and even damage to the probe components [17]. This variability can be addressed by monitoring water flow and conductivity for each stage, allowing performance to be calculated and/or normalized to a set of standard conditions. However, because permeate conductivity readings are typically taken on combined permeate, small defects in individual vessels can be masked by dilution. As such, conductivity monitoring by this method provides low resolution for integrity monitoring purposes, with facilities typically achieving LRVs between 1- and 2-log (90 to 99% removal). The State of California has granted 1.5-log virus removal for seawater desalination plants using RO in Carlsbad and Santa Barbara [41, 42] and 2-log virus removal for a seawater desalination plant in Avalon [43]. In these cases, despite the MFGM's requirement that a DIT have the resolution necessary to attribute the size of a defect and its restriction on using non-mass-based bulk parameters as surrogates for challenge tests, conductivity is used as a surrogate for DIT. For Carlsbad and Santa Barbara, 1.5-log removal is granted based on the requirement that the permeate from not more than eight (8) pressure vessels can be combined for a composite DIT [42]. For Avalon, 2-log virus credit is granted but every vessel must be tested individually [43]; individual vessel testing is discussed in Section 2.3.2.3.

2.3.2.3 Conductivity profiling and vessel probing

Unlike online conductivity monitoring, conductivity profiling does not provide real time (continuous) monitoring but is more sensitive to breaches in a system; profiling is often used to find the location of a breach in a compromised system [24]. Periodic conductivity profiling provides a greater degree of resolution by sampling the permeate streams of individual pressure vessels. Because vessels in

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the same stage should perform similarly, the routine collection of such data establishes a baseline for comparison and the identification of vessels with higher conductivity, or outliers in the data, that may indicate a defect (e.g., damaged O-ring).

Conductivity profiles are generated through the collection of conductivity readings from the permeate streams of individual vessels in each stage. If a conductivity profile indicates a defect may be present, the location of the defect within a single pressure vessel can be found through conductivity probing. For this process, a conductivity probe is introduced to the permeate tube of a pressure vessel, and conductivity is indexed along the length of the pressure vessel. A sharp increase in conductivity within the vessel would indicate the location of a defect in either the membrane or the interconnectors between membrane elements [44]. Conductivity profiles (e.g., as a DIT) can be generated in response to a change in combined permeate conductivity (e.g., as CIIM) as a way to identify an outlier element or generated as part of regular monitoring on a weekly, monthly, or quarterly basis. Currently, operators typically identify conductivity outliers through non-statistical means. Work is being undertaken to apply formal statistical limits to these profiles as a way to standardize the process and is discussed in detail in Section 2.3.2.4.

While conductivity profile generation is common and regulator-accepted, the process requires time and operator input to collect conductivity data from individual pressure vessels. Automation of profile generation can reduce the time required; the Yucaipa Valley Water District (YVWD), located in Southern California, has installed a novel automated conductivity profiling system capable of collecting conductivity data across an RO system as frequently as every two hours. The automated system is a solenoid manifold installed on a two-stage (52:20) 1,650 gpm RO train at the Wochoholz Regional Water Recycling Facility (WRWRF). The system is programmed to index pressure vessels one at a time to measure permeate conductivity across the entire system using only a single conductivity probe [20]. The combination of automated profile generation and the implementation of standardized statistical evaluation, as discussed in Section 2.3.2.4, has the potential as a substantially improved DIT resulting in higher LRVs without additional work by operators and at a low cost.

2.3.2.4 Statistical analysis of conductivity profiles and vessel probing data

There are three main statistical approaches that have been developed to better quantify LRVs based on conductivity monitoring as developed by Vickers [1]. The first statistical approach is to apply the central limit theorem and the "three-sigma rule", which establishes that in any normal distribution of data, 99.73% of samples should fall between three standard deviations (sigma) of the mean [45]. The second approach is to establish that the highest vessel conductivity of a stage should be no more than 50% greater than the stage's median conductivity. The final approach is to establish that skew, or the measure of distribution above and below the average, is an ideal or symmetric distribution around the average at zero, with a value of greater than +1 indicating that a defect may be present [46]. An example of the effect

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of an outlier data set can be seen in Figure 2-4. In the outlier data set graph (right), a single outlier is located outside of the three standard deviation limit (3σ). The outlier data has increased the average of the dataset without changing the median, and the skew is now positive as opposed to the zero skew in the normal distribution of data (left). If any of these conditions were calculated to be present when analyzing a dataset, it can be assumed that outlier data is present. The larger the outlier or the presence of multiple outliers would have an increased effect on the distribution of data as a whole.

Figure 2-4: The effect of an outlier data set on a normally distributed set of data [1]

From these approaches, a set of three rules was established to indicate conditions indicative of an integrity problem in a high-pressure membrane train:

- Permeate conductivity of a vessel is greater than or equal to the average plus three standard deviations per stage,
- Permeate conductivity of a vessel is greater than or equal to the median plus 50%, reduced to 30% following sensitivity analysis at the test site,
- The skew value per stage is greater than or equal to +1.0.

Data falling into one of these ranges would be considered a warning and reaching two of these ranges would be considered an alarm. However, these conditions are considered a starting point and would need to be tailored to each facility and membrane system, with sensitivity analyses performed to ensure that breaches are being identified correctly. Sensitivity analyses and correct identification of appropriate statistical limits will separate out nuisance alarms from true defects and be of vital importance to the efficiency of a treatment train using this process to maintain protection of human health [1]. It is important to note that these statistical limits apply to conductivity profiles generated from vessel probing (Section 2.3.2.3), as opposed to measurements gained from combined permeate (Section 2.3.2.2), and that the evaluation of conductivity profiles following these statistical rules formalizes the current operational practice. Typically, these profiles are generated and evaluated on a weekly, monthly, or quarterly basis to

ensure system integrity on an extended time scale. Automation of conductivity profile generation, as discussed in Section 2.3.2.3 and computer analysis by the statistical rules would allow for operational data on a much timelier basis [20].

As an example of such an approach, the YVWD verified the proposed statistical limits using conductivity profiles from August to September of 2016. Overall, the LRV ranged from 3.18 to 4.11 when used in combination with refined conductivity calculation methods that separates conductivity that results from "diffusion" versus a "defect", which is consistent with the pressure-based testing (i.e., dilution model) described in the USEPA MFGM [20].

To further explain how conductivity related to diffusion can be isolated from defects, an understanding of LRV calculation is required. The base calculation for LRV credits is given as Eqn. 2.2:

$$LRV = log(C_f) - log(C_p) \tag{2.2}$$

where the feed concentration (C_f) can be monitored as it enters the system and permeate concentration (C_p) can be calculated [5]. However, Eqn. 2.2 and the calculated LRV is more accurate if the flow weighted average of the individual stage permeate concentrations is used. Eqn. 2.3 shows the overall mass balance equation for an RO unit, and the weighted average calculation for permeate solute concentration of a multi-stage treatment system is shown in Eqn. 2.4 below [1]:

$$Q_f C_f = Q_p C_p + Q_c C_c \tag{2.3}$$

Where	Q_f	=	feed flow rate
	C_f	=	measured feed concentration
	Q_p	=	permeate flow rate
	C_p	=	measured permeate concentration
	Q_c	=	concentrate flow rate
	C_c	=	measured concentrate concentration

$$C_p = \frac{C_1 Q_1}{Q_p} + \cdots + \frac{C_n Q_n}{Q_p} \tag{2.4}$$

Where	C_1	=	Permeate concentration in Stage 1
	Q_1	=	Permeate flow rate in Stage 1
	Q_p	=	Membrane unit design capacity permeate flow rate
	C_n	=	Permeate concentration in Stage n
	Q_n	=	Permeate flow rate in Stage n

While use of Eqn. 2.4 gives a more accurate measure of permeate conductivity, this approach still suffers the drawback of not accounting for the two potential sources of conductivity in the permeate: 1) conductivity entering the permeate through diffusion across the membrane and thus not of pathogenic

concern; and 2) conductivity entering the permeate through a defect that would allow the passage of pathogens. This differentiation is done by separating the permeate mass flow rate (Q_pC_p) into two components: 1) the diffusion of conductivity through the membrane active layer, denoted by the subscript "diff"; and 2) conductivity transport or passage through a defect, denoted by the subscript "defect". Eqn. 2.5 shows this separation [1]:

$$Q_pC_p = Q_{diff}C_{diff} + Q_{defect}C_{defect} \tag{2.5}$$

The separation of the mass flow rate into these two terms allows for a modification of the dilution model equation used for pressure-based tests, as outlined in the MFGM. Equation 4.3 of the MFGM is used to determine the sensitivity of these pressure-based tests, shown below as Eqn. 2.6 [5]:

$$LRV_{DIT} = \log\left(\frac{Q_p}{VCF * Q_{defect}}\right) \tag{2.6}$$

Where   LRV$_{DIT}$ =   Direct Integrity Test sensitivity in terms of LRV

                 VCF   =   Volumetric Concentration Factor

                 Q$_p$ =   Membrane unit design capacity permeate flow rate

                 Q$_{defect}$ =   Flow across an integrity breach or defect

The Volumetric Concentration Factor (VCF), which is used to describe the increase in suspended solids when integrity is determined at the membrane [5], is considered equal to one (1) for RO membranes, as the mass quantity inherently accounts for the effect of concentration [1]. Further discussion of the VCF can be found in Section 2.5 of the MFGM [5].

Eqn. 2.5 can be rewritten and applied to vessels that are determined to be outliers, as shown in Eqn. 2.7. For this calculation, use of the median stage value is suggested to maintain a conservative approximation of conductivity. A higher standard deviation could be used on the basis that conductivity from multiple RO vessels fit within a normal distribution, as a higher diffusion component would result in a higher calculated LRV. However, exceeding two standard deviations is not recommended as it begins to exceed the limits of the central value theorem [1]. Regardless of the standard deviation chosen for calculations, the diffusion component of permeate conductivity will be substantially below conductivity associated with a defect.

$$\sum_{i=1}^{n} Q_{defect,n} = \frac{Q_{p,n}C_{p,n} - Q_{p,n}C_{diff,n}}{C_{defect,n} - C_{diff,n}} \tag{2.7}$$

Where $Q_{defect,n}$ = Flow through a defect in Stage n

$Q_{p,n}$ = Design capacity permeate flow for Stage n

$C_{p,n}$ = Permeate concentration at Stage n

$C_{diff,n}$ = Permeate concentration from diffusion in Stage n

$C_{defect,n}$ = Permeate concentration through a defect in Stage n

In practice, a simpler method of calculating concentration passing through a defect in a membrane is also possible; because outlier vessels should increase the average conductivity of the stage without affecting the median, it follows that a vessel with a defect would create a measurable increase in average conductivity in a stage while the median would remain the same. This theory allows Eqn. 2.8, the flow weighted average concentration calculation, to be modified to detect the increase in conductivity due to passage through a defect in a multi-stage system. For such an approach, average stage values are used for permeate concentration ($C_{p,n}$) and median stage values used for permeate concentration from diffusion ($C_{diff,n}$), resulting in Eqn. 2.8 [1]:

$$C_{defect} = \frac{(C_{p1} - C_{diff1})Q_1}{Q_p} + \cdots + \frac{(C_{p,n} - C_{diff,n})Q_n}{Q_p} \tag{2.8}$$

Where C_{defect} = Permeate concentration associated with a defect

$C_{p,1}$ = Permeate concentration at Stage 1

$C_{diff,1}$ = Permeate concentration from diffusion in Stage 1

Q_1 = Permeate flow rate in Stage 1

Q_p = Design capacity permeate flow

$C_{p,n}$ = Permeate concentration at Stage n

$C_{diff,n}$ = Permeate concentration from diffusion in Stage n

Q_n = Permeate flow rate in Stage n

A measurable difference across a stage would be indicative of a breach and result in a value for C_{defect} that could be used in for calculating an LRV for the defect using Eqn. 2.9, which is modified from Eqn. 2.2 [1]:

$$LRV_{defect} = \log(C_f) - \log(C_{defect}) \tag{2.9}$$

Vickers et al. [8] recently demonstrated that this approach coupled with conductivity profiling from vessel probing could identify integrity breaches allowing passage of virus, even when breaches were localized to one location within the RO train. The combination of automated conductivity profile generation as discussed in Section 2.3.2.3 and the new method of calculated LRV for the system at

YVWD resulted in an LRV increase from 1.59- to 3.19-log based on conductivity [1]. The calculations did vary with seasonal fluctuations in water quality, with summer months achieving credits around 3-log due to reduced feed quality, likely from warm temperatures, but winter months achieving up to 5-log removal [1]. While this variation is large, the lower end of the scale is still a substantial improvement upon the current credits given to conductivity measurements.

2.3.3 Total Organic Carbon Monitoring

Total organic carbon (TOC) monitoring is another common method of CIIM monitoring used by the reuse industry. However, TOC monitoring is not an accepted approach for DIT in the drinking water industry because naturally occurring TOC does not have a uniform size [47] that can be compared to the size of virus; the use of TOC as a monitoring method, therefore, does not meet the MFGM's sensitivity criteria.

In applications where TOC is an accepted approach for integrity verification, TOC monitoring involves the oxidation of carbon containing molecules in the water stream and the detection of carbon dioxide generated in the process. Naturally occurring TOC in reuse applications has been found to have a greater resolution than conductivity monitoring and is able to achieve an LRV of l.6-log without spiking [24]. Since the TOC in the feed and the permeate streams are at concentrations on different orders of magnitude, it is common for the implementation of two TOC analyzers – one able to detect higher TOC concentrations present in the feed stream and a second to monitor the lower TOC concentrations in the permeate stream. However, the cost of two instruments may limit some facilities from implementing TOC monitoring [17]. Like conductivity, TOC is not considered directly representative of virus transport through a membrane since a portion of organic matter is able to pass through the membrane by diffusion – a mechanism not available to viruses [18].

2.3.4 Sulfate Monitoring

Sulfate (SO_4^{2-}, Figure 2-5) has been identified as a potential naturally occurring surrogate for high pressure membrane integrity monitoring. Sulfate monitoring is an attractive surrogate because it is commonly present at high enough ambient concentrations in membrane feed waters, in part due to sulfuric acid dosing. Sulfuric acid is a common method of lowering the pH of feed waters to reduce the risk of forming calcium carbonate mineral scale [48]. Constant dosing of sulfuric acid has the added benefit of ensuring a more consistent feed concentration in addition to increasing LRVs.
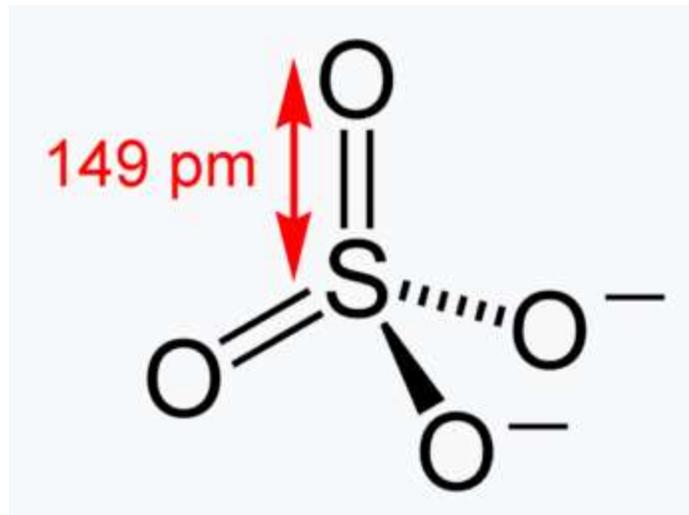
Figure 2-5: Sulfate ion

Online sulfate monitoring does exist but currently must be done by ion chromatography with instrumentation that is expensive and usually cost-prohibitive [49]. Collection of grab samples for ex-situ testing can be done for same-day analysis, but this method would not be able to provide real-time information on membrane integrity. Despite this, it has the potential to fulfill the requirement for a daily integrity test (DIT) [18]. A number of online and automated sulfate monitoring systems have been developed including the TitriLyzer and Envirolyzer (Applitek, Belgium), online IC (Metrohm, Switzerland) and others by Hach (USA), and Mettler Toledo. Among these the TitriLyzer can monitor up to eight streams sequentially and the Envirolyzer can monitor three streams sequentially although upgrades to automated sample valves can increase the number of streams that can be monitored with each system [50, 51].

Sulfate monitoring would be a conservative estimate of membrane integrity, however, due to the substantial size difference between sulfate ions and even the smallest virus particles. Sulfate also has the potential to pass through the membrane via diffusion as well as through defects. It may be possible to differentiate between sulfate diffusion and the passage of sulfate through defects using the method presented by Vickers for conductivity monitoring (i.e., profiling) [1], as discussed in Sections 2.3.2.3 and 2.3.2.4, with online monitoring of sulfate to increase removal credits for facilities using this method, however, no work has yet been performed to combine the methods.

Current work with sulfate monitoring that have not differentiated between diffusion and defect related sulfate concentrations has observed removals typically around 3-log (Figure 2-2 on page 4). Sulfate monitoring of the Western Corridor Recycled Water Scheme in Queensland, Australia observed 3-log reductions of sulfate in daily integrity testing. Removal may have been higher, but sulfate concentrations in the feed were not high enough to achieve more than 3-log [6]. A test performed at San

Diego's North City Water Reclamation Plant (NCWRP) observed sulfate rejections ranging from 2.4- to 3.1-log. While these results are in line with typical values, the data was collected over a 24-hour period and may not be representative of the LRVs the plant would achieve with more frequent monitoring [30].

The Heemskerk water treatment plant in the Netherlands was able to establish 3-log removal credits over a six-month monitoring period in 1998. This was lower than the tested MS2 removal of 4.8-log, demonstrating that the measurements were conservative but still above the 2-log LRV measured by conductivity removal [52]. These observed LRVs suggest sulfate could be a promising method of integrity monitoring; however, additional work is still needed to gain regulator acceptance and facility usage.

2.3.5 Strontium Monitoring

Strontium has also shown promise as a surrogate for integrity monitoring in high-pressure membrane systems because strontium is naturally found in wastewater at sufficiently high enough concentrations that additional spiking is not required. Several investigations involving strontium removal have been performed without accounting for diffusion related strontium transport, which conservatively represent the LRV this molecular marker can achieve. For example, investigations into strontium removal at the Orange County Water District Groundwater Replenishment System found that strontium removal was typically between 3.01- and 3.33-log, with minimal variation seen during the 24-hour sampling period [40]. Additional studies on strontium removal have found similar results, with ranges from 2.09- to 3.6-log removals [18, 53-55]. Strontium is also found at elevated concentrations in radioactive wastewater, with work being performed to assess removal by membranes across a wide range of conditions. NF experimentation performed on simulated low-level radioactive waste material found strontium rejections were near 100% at high pH, and rejections from 80-85% at more neutral pH levels [56]. Similar investigations found that strontium rejection reached a minimum of 97.2% rejection (approximately 1.98-log) at a pH of 5.0, where the membrane in use for the experiment reached its isoelectric point. Rejection values of 99.0% (2-log) and higher were observed below a pH of 5 and above a pH of 9.0. Experiments with spiked surface waters obtained 97.5% rejection (1.99-log), as well [57]. While the latter experiments are of relatively extreme conditions, they do support the evidence that strontium is a viable surrogate for membrane integrity monitoring. Online strontium analyzers are not currently available, limiting this technique's applicability for DIT or CIIM.

2.3.6 Sucralose Monitoring

The artificial sweetener sucralose ($C_{12}H_{19}Cl_3O_8$, Figure 2-6) is an organic compound that is widely used as a food additive, but it is not well adsorbed or metabolized by the human body, leading to

the majority of it being passed into wastewater [58] and subsequently into the environment due to incomplete removal during the wastewater treatment process [59, 60].
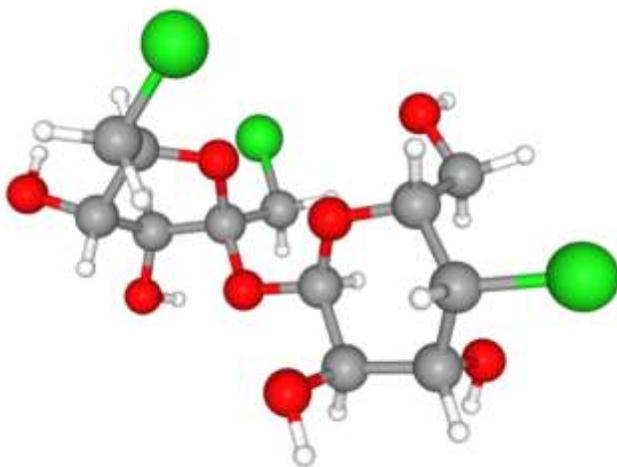

Figure 2-6: Sucralose molecule

Artificial sweeteners such as sucralose are currently being used as indicator compounds for the presence of wastewater in drinking water sources [61]. Sucralose has been found in surface waters in 27 European countries [62], as well as being shown to be widespread in the United States [62]. Because of its ubiquity in wastewater effluent, sucralose has promise as an integrity monitoring surrogate.

Like many of the other molecular markers discussed in this section, sucralose's low molecular weight (397.6 g/mol [63]) means it is able to diffuse through high pressure membranes, a method of transmission not available to much larger virus particles. Therefore, without isolating the effects of diffusion from the sucralose that may result from defects, the work that has been performed to date represents a conservative basis for assessing membrane integrity using sucralose as a molecular marker. As part of their investigations into chemical surrogates, Trussell et al. [18] investigated sucralose removals at a target feed concentration of 5 mg/L sucralose. Sucralose monitoring efforts were able to quantify 2.9-log removals across both unused and aged membranes, an increase of 1.0-log from conductivity monitoring done as part of the same experiment [18]. The Raw Water Production Facility in Big Springs, Texas saw removals of 2.43-log from facility influent to product water, with virtually no change from where the water entered the plant to entering the RO feed [12]. Sucralose monitoring does have the drawback of requiring LC-MS/MS analyses; the coordination, cost, and turnaround time required for analysis with contract or in-house labs limits the feasibility to conducting daily integrity testing. The cost of regular LC-MS/MS analysis may also deter smaller facilities from adopting regular sucralose monitoring, as well.

2.3.7 Fluorescence Excitation-Emission Matrix (EEM)

Excitation-emission matrix (EEM) is a fluorescence spectroscopy method that is used to characterize dissolved organic matter (DOM) in water systems. This technique is widely used for water quality monitoring [64, 65], effluent flow tracking [66], and in monitoring recycled water schemes [67] and has been investigated for its capacity as a high-pressure membrane integrity monitoring technique. An EEM is a three-dimensional contour plot of thousands of data points generated by measuring fluorescence intensity across a range of excitation and emission wavelengths [68]. DOM, which is being measured, is a heterogeneous mixture of aromatic and aliphatic hydrocarbon structures containing different functional groups [69]. However, only a small fraction of DOM molecules have the ability to absorb wavelengths greater than 200nm (chromophoric DOM (CDOM)), and only a fraction of CDOM will fluoresce (FDOM); less than three percent of absorbed photons are emitted as fluorescence [70]. As such, EEM analysis should be done with great caution and oversimplifying data from such a small subset of DOM particles risks bias in the analysis, masking integrity issues [68]. Research on EEM as a monitoring technique has found a calculated LRV of 3-log (99.9%) when combined with size exclusion chromatography [16]. A recent review by Yoon [16] concluded that use of natural fluorescence is unlikely to yield LRVs greater than conductivity measurements. Natural DOM also fails to meet the MFGM's sensitivity requirement for a DIT method as the size of DOM is not uniform and therefore not comparable to the size of a virus. In addition, there is not currently a standardized method of interpreting EEM and additional work is needed to verify its applicability to high-pressure membrane monitoring.

2.3.8 Nanoparticles

Nanoparticles are becoming increasingly accepted as potential surrogates, because they can be produced at sizes similar to the smallest virus particle and remove some of the risk involved in challenge tests using live MS2 bacteriophage. A wide range of potential nanoparticles exist, including fluorescent micro- and nano-particles [29, 33, 34, 71-74], gold nanoparticles [73], and magnetic nanoparticles [75, 76]. While these particles offer the potential for real-time integrity monitoring, further investigation needs to be done on the process. For example, the effects of solubility, surface chemistry, agglomeration and other factors influencing rejection is still largely unknown as most challenge tests to date have not considered their effects.

It has been reported that some nanoparticles aggregate and foul the surface of membranes, providing overestimated calculations of LRVs and system integrity [77]. If the fluorescent markers are improperly attached to the nanoparticles, there is a risk of the fluorescence leaching from the nanoparticle's surface into the surrounding waters, again providing incorrect estimates of membrane integrity [7]. Production of the large amounts of fluorescent nanoparticles needed for full scale

monitoring would be expensive, particularly for smaller facilities, despite the relative ease of fluorescence monitors [17].

There is additional work needed to determine the fate and toxicity of the synthetic or engineered nanomaterials in the environment; such information in relation to nanoparticles is largely unknown with the exception of common inorganic nanoparticles (i.e., TiO_2) [78]. The use of magnetic nanoparticles could potentially address many of these concerns, as they could potentially be recovered for reuse, but testing is limited and has largely been performed on UF membranes [76]. The cost of implementing the required instruments for full-scale implementation of magnetic nanoparticle detection and recovery would be of considerable cost to facilities.

Despite this, nanoparticles have shown the ability to provide the required sensitivity for high pressure membrane integrity monitoring. Silver nanoparticle feed concentrations of >8 mg/L were able to obtain maximum LRVs of 2.57-log [79], though the detection mode was limited to off-line analysis. A more recent test was able to calculate an LRV of >5-log at a pulsed feed concentration of approximately 2 mg/L [6]. However, this method also required testing to be done off-line.

2.3.9 Adenosine Triphosphate (ATP)

Adenosine Triphosphate (ATP) is a nucleotide that transfers energy within cells, present in all living cells, and degrades rapidly when cells die [80]. ATP measurements are useful as surrogate measures of all active and unculturable microbial cells, thus providing better estimates of biomass than herotrophic plate counts [81]. This makes ATP measurement a useful surrogate for membrane integrity monitoring. Total ATP in a water sample is the sum of cellular ATP (cATP) that is still bound within living cells combined with extra-cellular ATP (free ATP) from dead or lysed cells. Free ATP, with a molecular weight of 507 g/mole, should theoretically be well removed by RO membranes with a molecular cutoff of 150 Da or lower [82] and is abundant in feed waters [40].

Currently ATP is used as a biomass indicator in RO systems to quantify biomass on membrane surface, diagnose biofouling, measure biomass in feedwater, and as a biomass parameter in bacterial growth potential measurements. Up until recently, ATP levels could not be measured online and ATP concentration measurements relied on a semi-rapid (15 minutes)bioluminescence method in batch mode, with the level of light output detected correlating directly to a sample's ATP concentration [12]. The method does not work for high ionic strength waters, such as seawater, due to inhibition of the ATP reaction and interference with background luminescence [80]. Waters at the Raw Water Production Facility were found to have substantial reductions in ATP levels across the RO system, with permeate samples falling below 0.1 pg/mL of cATP from approximately 25 pg/mL in the feed [12]. Similarly, work done as part of WRRF Reuse-12-07/WRF 4757 calculated 2.52-log reductions in ATP levels across an intact system [7]. ATP measurements also showed sensitivity to common integrity damage tests, with

28

large reductions in LRV from introduced damage [7]. More recently, several companies have offered online ATP monitoring devices such as the Hach's (Loveland, CO) EZ-ATP Online Microbial Analyzer. In practice, such a device could be used to monitor ATP in near-real time as a membrane integrity monitoring approach. Orange County Water District has reportedly been evaluating online ATP monitoring for integrity monitoring of RO systems at their Groundwater Replenishment System Advanced Water Purification Facility.

2.3.10 Additional Methods

Jacangelo et al. [7] performed a comprehensive review of proposed membrane integrity methodology including approaches that were in development prior to 2019, and generated a comprehensive summary table in their report. The lengthy list of 'monitoring techniques' is not included herein, however it is worth noting that substantial effort has been put towards developing more effective integrity monitoring approaches. Many of the methods in the Jacangelo et al. [7] work are not included in this review due to high cost of implementation, impracticality for large-scale membrane systems, and/or the requirement of additional research and development prior to deployment.

Huang et al. [83] evaluated the use of flow cytometry (FCM) among other pathogen quantification methods as a tool for indirect integrity monitoring as it measures total viruses particles. FCM measurements at a water reuse facility employing MF-RO indicated that approximately 3-log removal could be quantified on the combined MF-RO system using FCM measurements. In addition, the researchers evaluated dynamic light scattering (DLS) as a method for submicron particle counting. Both FCM and DLS methods were reported as relatively expensive relative to other CIIM methods (i.e., conductivity and TOC) and required additional development for deployment.

Hornstra et al [13] evaluated the removals of naturally occurring viruses in fresh surface water across RO membranes as a method of DIT. Surface water analyses identified two species that were at high concentrations in the six European surface waters being tested. Once identified, qPCR assays were developed to allow testing for the selected natural viruses. Hornstra et al found LRVs of more than 6.0-log for both natural virus species across intact membranes [13]. Both natural viruses also showed large reductions in LRVs when damage was intentionally introduced into the system. The identification of natural viruses in an RO system would allow for similar monitoring sensitivity as achieved by MS2 without the costly addition of production or the risks associated with the use of large amounts of the bacteriophage. The method requires further development, as natural viruses remain largely unidentified in surface water [13], and the actual concentrations of natural viruses may be site-specific.

Commercially available, online and semi-continuous water quality monitoring devices have become more prevalent over the past several years. Several commercial systems have been developed for detection of anomalous water quality events in drinking water distribution systems and wastewater

collection systems including s::can, LiqID, Kando, or software coupled to water quality measurements such as CANARY. Based mainly on spectrophotometric analysis, these systems are typically used to detect changes in water quality, alerting operators to potential water and wastewater system upsets. Newhart et al. [84] presented a good review of real-time water quality monitoring to aid in decision making at wastewater treatment facilities; combining water quality monitoring data with machine learning may aid in the rapid detection of high-pressure membrane integrity issues and potentially, higher LRVs.

2.4 Summary of Findings

Historically, drinking water production facilities employing NF or RO rely on conductivity monitoring to obtain a base-level LRV credit of 1.0- to 2.0-log. A substantial amount of fundamental and applied research has been undertaken to develop DIT and CIIM approaches to improve integrity monitoring and obtain greater LRVs in accordance with the MFGM. Because the LT2ESWTR does not require the use of a particular DIT for rule compliance, but stipulates that any test used meet must the specified performance criteria for resolution, sensitivity, and frequency, researchers and practitioners have focused on alternative surrogate markers (e.g., molecular markers) that meet the requirements of the MFGM and result in appropriate LRV credits. The MFGM also did not consider the concept of multiple location DIT such as those explored by Vickers et al. (2018). The work done at YVWD has shown that multiple location DIT has the potential to more accurately describe removals than traditional methods of measuring combined permeates, thus addressing a traditionally overlooked method of integrity characterization. The objective of this literature review was to screen pertinent sources of information to identify promising membrane integrity monitoring approaches to be evaluated through experimentation during the course of this project.

Various indigenous and exogenous molecular markers have been evaluated for use in DIT and CIIM of RO and NF membranes. Several markers were identified to yield quantifiable LRVs of 3-log or higher including certain fluorescent dyes, sulfate, strontium, and wastewater derived organic contaminants (sucralose). Considering the practicality (e.g., cost, measurement ease) and regulatory (e.g., resolution, sensitivity) requirements associated with marker adoption, it appears feasible to achieve close to 3-log removals through either dosing and/or monitoring of an appropriate fluorescent dye (e.g., uranine) or sulfate.

Although molecular markers have been identified that can be used in DITs or CIIM to quantify LRVs greater than those obtained through conductivity monitoring, the findings of this literature review suggest that routine monitoring of these markers is unlikely to yield LRVs that are much greater than 3-log. This is largely due to the fact that diffusion of these markers through the membrane constrains measurement of LRVs to around 3-log, even with no loss of integrity. As a result, several analogous approaches to the dilution model correction applied to pressure-based DITs outlined in the MFGM have

been developed. One such method developed by Vickers [1] uses statistical analysis to differentiate between diffusive and advective solute mass transfer, and calculates LRVs based on permeate conductivity resulting from an integrity breach. The combination of automated conductivity profile generation and this monitoring approach for the system at YVWD resulted in an LRV increase from 1.59- to 3.19-log based on conductivity[1]. An analogous yet less developed concept also identified used a membrane imperfection model [21] to assess integrity through permeate monitoring. Combination of one of these approaches with measurement (i.e., profiling) of a more sensitive molecular marker (e.g., fluorophore, sulfate) that by itself yields quantifiable LRVs greater than 3-log, should substantially improve the quantifiable resolution.

2.5 Conclusions

Despite the ability of RO, and to a lesser extent NF, to act as a robust barrier to dissolved solids (e.g., sodium, chloride), high-pressure membrane systems are routinely granted conservative pathogen LRVs by regulators (1- to 2-logs) when using the integrity monitoring guidelines outlined in the MFGM. A substantial amount of work has been performed to demonstrate higher LRVs including application of sophisticated and sensitive analytical techniques, statistical data analysis, and the use of membrane transport models. The main challenges associated with successful adaption of these approaches are 1) finding a molecular marker that meets the sensitivity requirements of a DIT as specified in the MFGM, meaning its size can be compared directly to that of virus; 2) finding a molecular marker and/or analytical approach that meets the resolution requirements of the MFGM and, ideally demonstrate at least 4-log removal; 3) applying a marker monitoring approach to a system which could potentially include many pressure vessels on a daily or semi-continuous basis; and 4) obtaining regulatory approval.

Following this literature review, several methods were identified for further testing. In depth analysis and application of the statistical methods of determining LRV using conductivity profiling data, as presented in Section 2.3.2.3, is discussed in detail as part of Chapter 3. Results can be found in Chapter 4. Several chemical markers were identified for their promising results in pilot scale membranes and were evaluated for their applicability to a closed circuit desalination (CCD) system to compare the LRV achieved with a traditional membrane system. A discussion of the CCD system as well as testing methods can be found in Chapter 3, and results can be found in Chapter 4.

CHAPTER 3

METHODS AND MATERIALS

3.1 Statistical Methods of LRV Calculation Based on Conductivity Profiling

Conductivity measurements are a common method of integrity monitoring for high-pressure membranes for their relatively low cost, ease of implementation, and ready acceptance by regulators. However, they rarely receive above 2.0-log credits and little research has been performed to improve methods of conductivity monitoring. The literature review that was completed as part of this thesis, which can be found in Chapter 2, identified a novel method of utilizing conductivity data in combination with the dilution model, an established method found in the MFGM, to drastically improve LRV results. The application of statistical analysis to already common profile generation conducted by utilities standardizes the method of identifying outlier vessels and potentially allows for early detection of compromised vessels within a full-scale RO/NF train. Vickers' own analysis of train data from YVWD resulted in an increase of LRV from 1.59 to 3.19-log [1]. In order to verify the applicability of the Vickers' statistical method of determining LRVs based on conductivity monitoring, conductivity profile data was acquired from multiple water treatment sites in the United States and analyzed using the statistical rules set forth by Vickers. In order to verify the analysis method's applicability to a wide range of treatment needs, care was taken to ensure the sites analyzed had different sizes of trains, as well as different sources of feed water.

Data provided as part of WRRF Project 4958 was analyzed using statistical analysis of conductivity profiles. A spreadsheet developed and shared by Dr. Jim Vickers was modified to data provided, which included flowrates, conductivity measurements, stage level pressure, and temperature; however, a majority of this data was not necessary for the statistical evaluation of the train. As discussed in Section 2.3.2.4 of the literature review, the conductivity profiling method established three rules to indicate conditions indicative of an integrity problem in a train:

- Permeate conductivity of a vessel is greater than or equal to the average plus three standard deviations per stage,
- Permeate conductivity of a vessel is greater than or equal to the median plus 50%, reduced to 30% following sensitivity analysis at the test site,
- The skew value per stage is greater than or equal to +1.0.

As such, permeate conductivity data for each vessel was gathered, an example of which is shown in Table 3-1 below.

Table 3-1: Conductivity readings (µS/cm) by vessel

Stage 1				Stage 2	
23.7	22.9	22.3	21.6	67.8	49.9
21.9	22.1	22.7	23.3	55.8	54.4
21.3	23.3	24.0	24.5	54.8	54.0
24.8	24.8	23.2	21.7	53.5	54.7
24.9	22.6	21.9	22.2	58.1	54.6
25.5	24.6	23.0	23.5	53.3	57.9
23.1		24.2		52.1	

The data set was used to calculate the average permeate conductivity, standard deviation, skew, median, minimum, and maximum for each stage. This data was used to calculate if individual vessels activated alarms based on the established rules. Since site-specific sensitivity analysis had not been performed, multiple levels of alert were set for the second established rule: separate alerts were set for the median plus 30%, 40%, and 50%. In the calculations shown in Table 3-2 below, values were calculated for the dataset shown in Table 3-1; for this dataset there was an activated alarm for skew in the second stage, highlighted in red.

Table 3-2: Vessel Alarm Calculations

Conductivity Calculations			
Parameter	**Units**	**Stage 1**	**Stage 2**
Average Permeate Conductivity	µS/cm	23.2	55.5
Standard Deviation	µS/cm	1.2	4.3
Median Permeate Conductivity	µS/cm	23.2	54.6
Minimum Permeate Conductivity	µS/cm	21.3	49.9
Maximum Permeate Conductivity	µS/cm	26	68
Average +3 Standard Deviations	µS/cm	27	68.3
1.3*Median	µS/cm	30	71
1.4*Median	µS/cm	32	76
1.5*Median	µS/cm	35	82
Skew	---	0.22	2.10
Activated Alerts			
COUNT Avg +3*Standard Deviations	Vessels	0	0
COUNT 1.3*Median	Vessels	0	0
COUNT 1.4*Median	Vessels	0	0
COUNT 1.5*Median	Vessels	0	0
Skew Greater Than or Equal to 1.0	---	0	Activated

As discussed in Section 2.3.2.4, this single activated alert would be considered a warning that a potential fault existed in the system and the activation of a second alert would be considered an alarm. At that point, the outlier vessel(s) would be individually tested to locate and address any defects.

While this analysis is useful for potential early warnings of integrity breaches or more accurate identification of outlier vessels, it does not provide an LRV. For this, additional calculations are required. An example of LRV calculations using the equations discussed in Section 2.3.2.4 is shown below in Table 3-3.

Table 3-3: Log Removal Value Calculations (manual input values highlighted in light yellow)

Parameter	Units	Stage 1	Stage 2	Train
Feed Conductivity	µS/cm			1,097
Kfactor	mg/L/µS/cm			0.55
Feed TDS	mg/L			603
Log Feed TDS	---			2.78
Permeate flow	gpm	714	350	1,064
Average Permeate Cond.	µS/cm	23.2	55.5	33.8
Average Permeate TDS	mg/L	12.8	30.5	18.6
Log Permeate TDS	---	1.11	1.48	1.27
Traditional LRV	---			1.51
Median Permeate Conductivity	µS/cm	23.2	54.6	33.5
Median Permeate TDS	mg/L	12.7	30.0	20.1
Adjusted Permeate TDS	mg/L	0.04	0.47	0.18
Adjusted Permeate Log TDS	mg/L	-1.4	-0.3	
LRV	---	4.22	3.11	
Beta	---	16,778	1,285	
Percent Removal	%	99.994	99.922	99.970
Adjusted LRV	---			3.53

For this analysis, the feed conductivity of the train is required, as well as permeate flow rates for each stage and the combined flow rate (labeled as train flow rate). Conductivity is used as a surrogate for TDS using Eqn. 3.1:

$$C_f = Cond_f * K_f \tag{3.1}$$

Where C_f =   Feed concentration in TDS

             $Cond_f$ =   Feed conductivity

             K_f =   Kfactor

The Kfactor (K_f) is typically established through water quality measurement in a system, but for this analysis, a constant of 0.55 mg/L/µS/cm was used. The same conversion is performed on the average permeate conductivity for each stage, which were calculated as part of the vessel alarm calculations (see

Table 3-2). Average permeate conductivity for the combined permeate stream is calculated by combining the flowrate from both stages as well as the respective permeate conductivities using Eqn. 3.2. The same process is used to calculate average permeate TDS for the combined permeate.

$$C_{p,system} = \frac{C_{p1}Q_{p1}}{Q_{p,system}} + \frac{C_{p2}Q_{p2}}{Q_{p,system}} \qquad (3.2)$$

Where $C_{p,system}$ =   Permeate concentration for the combined permeate

               C_{p1} =   Permeate concentration for the 1st stage

               Q_{p1} =   Permeate flow for the 1st stage

               C_{p2} =   Permeate concentration for the 2nd stage

               Q_{p2} =   Permeate flow for the 2nd stage

               $Q_{p,system}$ =   Combined permeate flow

The log of the average permeate TDS is subtracted from the log of the feed TDS to calculate a traditional conductivity-based LRV; in Table 3-3 that value is 1.51-log. However, as discussed in Section 2.3.2.4 of the literature review the conductivity profiling method separates out the permeate mass flow rate (Q_pC_p) into two components via Eqn. 3.3:

$$Q_pC_p = Q_{diff}C_{diff} + Q_{defect}C_{defect} \qquad (3.3)$$

For this equation, the average concentration in the permeate (C_p) is calculated using Eqn. 3.2. The diffusion of conductivity through the membrane active layer (C_{diff}) is accounted for by the median permeate concentration. Subtracting the median permeate concentration for a stage (C_{diff}) from the average permeate concentration for the same stage (C_p), in combination with stage and train flow rates, the permeate concentration that can be associated with a defect (C_{defect}) is determined. If the C_{defect} for a specific stage is less than zero, the stage is considered intact and given a 5.0-log credit. If the C_{defect} for a stage is greater than zero, the log of the adjusted permeate value is taken and that value is subtracted from the log of the feed concentration in the modified version of the LRV calculation presented in Eqn 3.4:

$$LRV_{defect} = \log(C_f) - \log(C_{defect}) \qquad (3.4)$$

Percent removal is calculated based on the stage-specific LRV calculation and a flow-rated percent removal is calculated for the entire train. This percent removal is then transformed into a train level adjusted LRV. In Table 3-3 above, the adjusted LRV value is 3.53-log. While this is still below the theoretical removal capabilities of a membrane system, it is a substantial improvement on the LRV calculated using the traditional conductivity method.

3.2 Application of selected molecular markers to a Closed Circuit Desalination (CCD) system

The CCD experiments were performed using a Desalitech Closed Circuit Desalination (CCD) system that was fitted with three 8040 (8 inch by 40 inch) spiral wound membrane elements. The first experiment was done on NF-270 membranes and the second on NF-90 membranes, with molecular weight cutoffs of 340 and 180 g/mole, respectively [85]. The CCD system was located at the WE2ST Water Technology Hub, a research center operated by the Colorado School of Mines in Denver, Colorado. The CCD system was similar to what is seen in Figure 3-1 on the next page, with the pressure vessels and the recirculation aspect of the system contained within a temperature controlled shipping container. The feed tank was located within the WE2ST building, and the permeate and concentrate tanks located next to the shipping container.

Prior to operation, the feed tank was filled with 1,700 gallons of Denver tap water and dosed with sodium metabisulfite (antiscalent) for chlorine removal followed by the addition of uranine, rhodamine B and strontium chloride hexahydrate. The fluorescent markers uranine and rhodamine B were chosen to be evaluated in the CCD because of the high LRVs obtained in previous studies, which are discussed in Section 2.3.1. Strontium similarly demonstrated promising LRV results, discussed in Section 2.3.5, and potentially would require no additional spiking in wastewater thus minimizing costs to facilities that choose to implement strontium as a monitoring technique. The target dose amounts for each membrane system experiment are presented in Table 3-4.

Table 3-4: Feed Tank Target Dosing Rate for Chemical Markers

Chemical Marker	Chemical Formula	Target Tank Concentration (mg/L)	
		NF-270	**NF-90**
Uranine	$C_{20}H_{10}Na_2O_5$	0.5 mg/L	0.5 mg/L
Rhodamine B	$C_{28}H_{31}ClN_2O_3$	0.5 mg/L	0.5 mg/L
Strontium Chloride Hexahydrate	$H_{12}Cl_2O_6Sr$	2.0 mg/L	2.0 mg/L
Sodium Metabisulfite	$Na_2S_2O_5$	3.0 mg/L	3.0 mg/L

The system was operated at a permeate flux of approximately 12 gfd (gallon/ft^2-d; 20 liter/m^2/hr (LMH)) during the experiments. The system was operated up to a recovery of 95%, whereupon the concentrate was purged from the system into an external combined concentrate tank (E in Figure 3-1) and the process was begun again. This process was run twice, with samples being taken at recoveries of 50%, 75%, 80%, 85%, 88%, 91%, 93%, 95% at three sampling locations: the influent stream (A), the concentrate stream prior to mixing (B) and the permeate stream (C), as presented in Figure 3-1. During operation, all generated permeate was collected in a combined permeate tank (D); after each experiment was completed, a sample was collected from this tank as well as the combined concentrate tank (E).
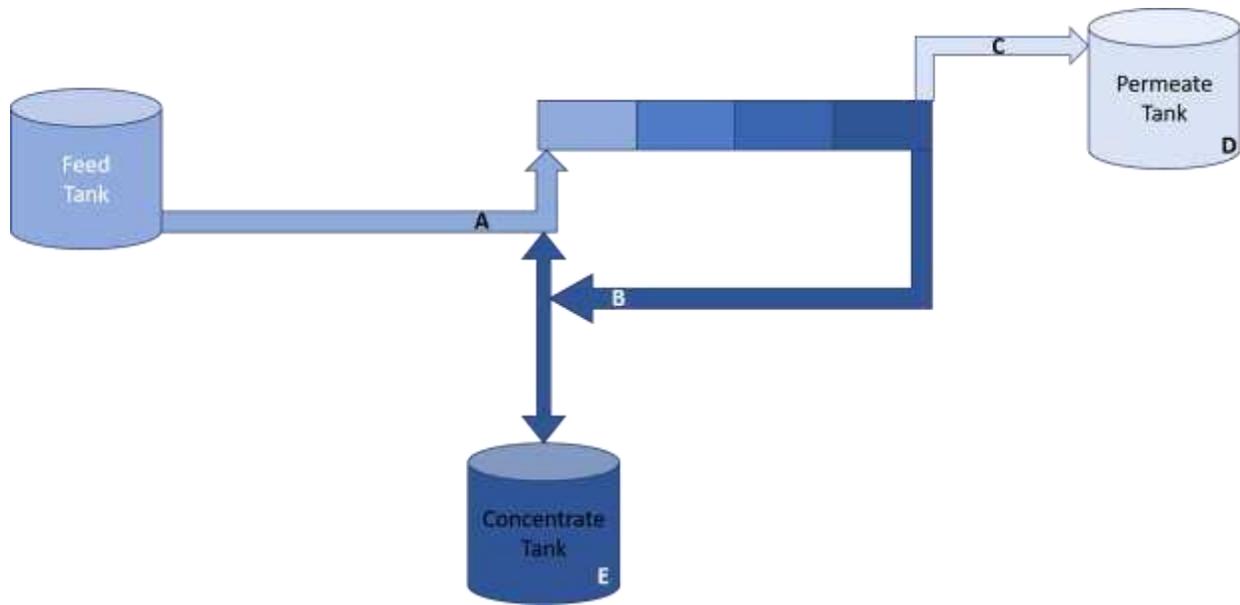
Figure 3-1: Industrial Closed Circuit Reverse Osmosis System

Sample collection at the selected recoveries allowed for an in depth look at how markers behavior differed in the CCD system with the recirculation of the concentrate. Samples from the combined permeate and average influent concentrations for each marker were used to calculate a typical LRV. However, this combined permeate includes permeate generated from a wide range of feed water concentrations, from an unconcentrated feed at the beginning of the recirculation process to a feed water mixed with highly concentrated concentrate, which could alter marker behavior substantially. Therefore an LRV was calculated for each of the representative recoveries in addition to the combined permeate. In order to understand how the feed concentration (C_f) changed as recirculation occurred, flowrate data from each of the streams (permeate, concentrate, and influent) were graphed. By design, permeate flow remained at or near 10 gpm because the system operates at a constant flux (12 gfd for these experiments), though flow near the beginning of an experiment can fluctuate as the CCD reaches equilibrium. At equilibrium, the concentrate and influent flowed at 25 and 10 gpm, respectively, for the experiments conducted. Based on these values, it was determined that the feed concentration for any given recovery rate was a mixture of 71% recirculated concentrate (C_c) and 29% fresh influent (C_i). Based on these percentages a new LRV calculation, Equation 3.5, was used for calculating LRVs for each recovery setpoint.

$$LRV = \log(0.71(C_c) + 0.29(C_i)) - \log(C_p) \qquad 3.5$$

3.2.1 Chemical Analysis Methods

Collected samples were analyzed for TOC and total nitrogen using a Shimadzu TOCV-TNM-LCSH with a limit of quantification (LOQ) of 0.17 mg/L. TOC/TN analysis samples were prepped by inserting approximately 24 mL of each unfiltered sample into a glass vial, which was then acidified with 4 drops of concentrated hydrochloric acid (HCl). Strontium was analyzed using a PerkinElmer Optima 8300 ICP-OES with an LOQ of 3 µg/L (0.003 mg/L). Approximately 10 mL of sample was passed through a 0.45 µm filter and placed into a 15mL conical tube and then acidified with 200 µL of concentrated nitric acid (HNO_3).

Fluorescence was analyzed with absorbance spectra on the Horiba AquaLog spectrofluorometer system. Following sample prep for ICP, approximately 3.5 mL of sample was passed through a 0.45 µm filter into a VWR Spectrophotometer Cell, or cuvette. The cuvette was loaded into the spectrofluorometer system in a consistent manner and percent transmittance was recorded every 3nm from 239nm to 800nm in order to capture the absorbance intensity of Uranine and Rhodamine B (491 and 554 respectively). Transmittance was converted into absorbance via Eqn. 3.5, which was then used to calculate actual concentration using Beers-Lambert Law (Eqn. 3.6):

$$A = -\log(T) \tag{3.6}$$

$$A = \varepsilon cl \tag{3.7}$$

Where   T   =   Transmittance (%)

            A   =   Absorbance

            ε =   Molar absorption coefficient (M^{-1} cm^{-1})

            c   =   Molar concentration (M)

            l   =   optical path length (cm)

Eqn. 3.6 was modified to solve for molar concentration as shown in Eqn. 3.7:

$$c = \frac{A}{\varepsilon l} \tag{3.8}$$

The optical path length is defined as the length of the cuvette used for the absorbance measurement and was assumed to be 1 cm, the typical cuvette measurement. The molar absorption coefficient for uranine is affected by impurities and pH of the solution. However, spectrophotometric analysis of Uranine by Mota et al found that the molar absorbtion coefficient at a pH of 7 was 65,000 $M^{-1}cm^{-1}$ [86]. Rhodamine B has a molar absorbtion coefficient of 106,000-108,000 $M^{-1}cm^{-1}$ [87], so a mid-range of 107,000 $M^{-1}cm^{-1}$ was used. Molar concentration was then used to calculate concentration in mg/L using the molecular weight of both compounds (376.26 g/mole for Uranine and 479.02 g/mole for Rhodamine B). Results from the CCD experiments can be found in Section 4.3.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Following a thorough literature review (Chapter 2), several promising integrity monitoring techniques were evaluated. The first of these methods was a statistical evaluation of conductivity profiling data for full scale facilities. Profiling data generated from multiple full scale water treatment facilities with a variety of water sources was analyzed to determine the potential of statistically generated LRVs. By comparing the LRV generated from statistical analysis with an LRV generated with the traditional conductivity method, the increase in LRV as well as the method's sensitivity to breaches, changes in conditions, and user error can be determined. Because the method must have a statistically significant number of vessels in the conductivity profile in order to work, this analysis method must be done at full scale, and is not applicable to pilot scale systems. If such analysis were able to demonstrate improved LRVs from conductivity alone, exploration of alternate markers (i.e., TOC, sulfate, etc.) could be pursued to provide facilities greater flexibility in their integrity monitoring options.

The literature review also identified several molecular markers that have demonstrated large LRV results, though widespread acceptance is an ongoing process. Quantifying the LRV these markers are able to achieve is a major goal of this work. The application of the chosen markers with the CCD was chosen as a method to determine an LRV for these markers when used with NF membranes, as the use of combined permeate and influent concentration could be considered comparable to a pilot-scale membrane test. This had the additional benefit of testing the application of these markers to a new high pressure membrane system. The unique nature of the CCD could result in altered rejections of a marker chosen to monitor integrity. Differences in marker behavior when used in a CCD would need to be well understood, including LRV, before being used as an integrity monitoring method for water treatment.

4.2 Statistical Methods of LRV Calculation Based on Conductivity Profiling

As discussed in Section 2.3.2.4 of the literature review, the combination of conductivity profiling coupled with statistical evaluation has shown great promise as a method of integrity monitoring. Conductivity monitoring is already a common practice in utilities, and instrumentation for manually generated profiles is inexpensive. While Vickers et al have also proposed the automation of these profiles [20], as discussed in Section 2.3.2.3, the reliability of the method is currently being examined. A discussion of the methodology used to evaluate the profile data can be found in Section 3.1. The data evaluated in this section was provided by two utilities in partnership with The Water Research Foundation (WRF) Project 4958. The utilities had different source waters (i.e., groundwater, wastewater) which allows for the evaluation of the statistical analysis method on multiple types of membrane treatment

systems. Both facilities are located in California, where water scarcity and saltwater intrusion of aquifers have made water reuse a priority. Higher LRV credits for RO and NF treatment will reduce the burden on utilities under regulations that are increasingly strict in the pursuit of protecting the environment and human health.

4.2.1 Mocho Groundwater Demineralization Plant (MGDP)

For the first set of data, RO train profile data was obtained from the Mocho Groundwater Demineralization Plant (MGDP) in California. The plant treats up to 7.7 million gallons of brackish groundwater per day, which is then blended with other water sources to supplement the water in California's Zone 7 water district [88]. The plant has four trains, that each contain two stages; the first stage has 26 vessels and there are 13 vessels in the second stage. Each train can produce approximately 1.5 million gallons per day at a typical recovery rate of 80%. The plant has been in operation since 2009, and data was provided from profiles taken between 2010 and early 2020.

A comparison between the traditional use of conductivity for integrity monitoring (measuring conductivity in feed and combined permeate), and the conductivity profiling method (using statistical analysis presented in Section 2.3.2.4) is presented in Figure 4-1 on the next page. Data in Figure 4-1 shows the ten-year average LRV for the four trains at MGDP as a box and whisker plot. The conductivity profiling method of LRV calculation resulted in a substantial increase in LRV as opposed to the traditional conductivity calculation. For this location, calculating LRV using the membrane feed water and combined permeate (orange) was unable to achieve above 2.0-log over the entire ten-year time span of operation, well below the likely removal capability of an intact system. Additionally, while there were conductivity datasets where the traditional conductivity calculation resulted in a complete loss in log removal credits, these were often associated with large decreases in feed conductivity which may be a result of damaged equipment. For Trains 2 and 3, when the traditional conductivity method reached 0-log credits, both maintained an average LRV above 3.5-log using the conductivity profiling method. Determining removals via conductivity profiling yields a value that is more indicative of the true performance of a high-pressure membrane system for virus removal.
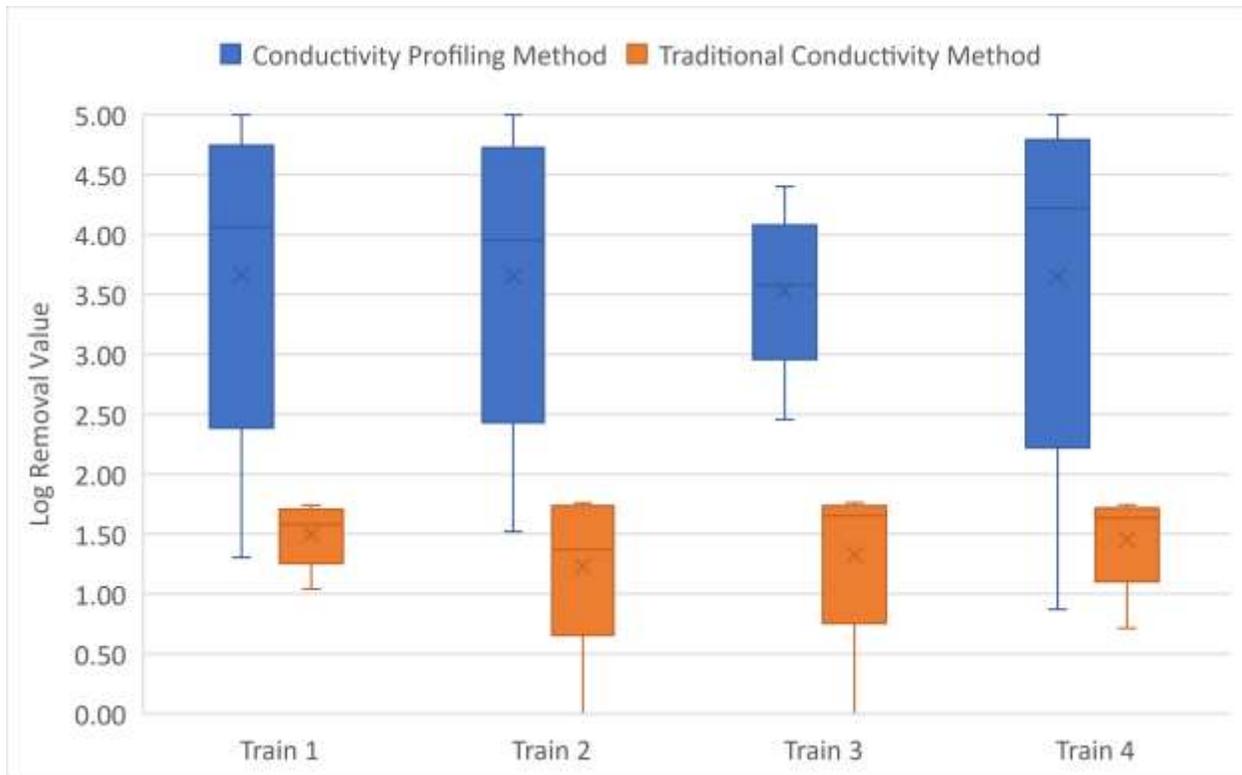
Figure 4-1: Average LRV Calculations for MGDP

Analysis of Train 1, which is shown in Figure 4-2, uncovered a sharp decline in performance when using the statistical method presented by Vickers between 2011 and 2012, which is boxed in red in Figure 4-2 below. This steep decline resulted in LRVs below 1.5-log, which was lower than the value calculated using the traditional conductivity method. The traditional conductivity method of LRV calculation showed no corresponding response to potential issues during this period, showing no sensitivity to the potential breaches and potential passage of pathogens. No information was provided by the utility to indicate that a breach or integrity issue occurred during this time period, however. For this location, the conductivity profiling method appears to be a more sensitive integrity monitoring approach.
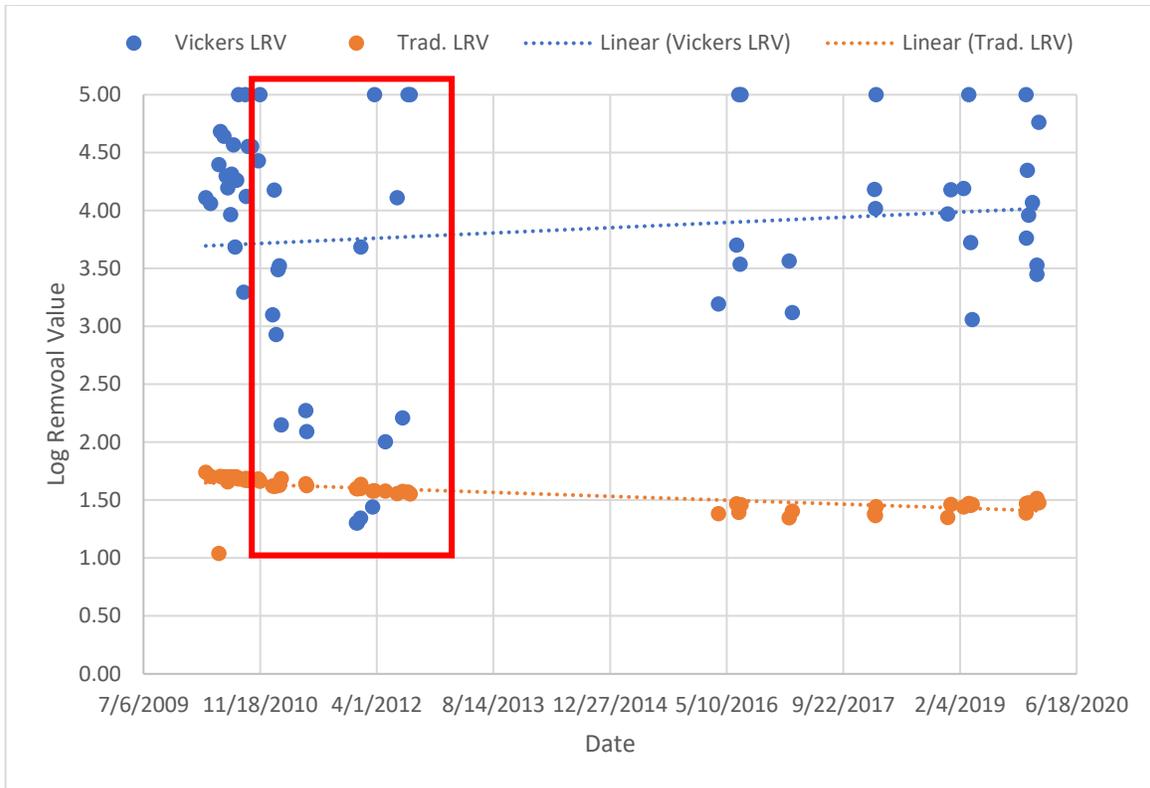
Figure 4-2: Train 1 LRV Calculations

Analysis of the remaining trains at MGDP can be found in Appendix A, but trends discovered from their analysis will be discussed here. Train 2 had similar lifetime performance to Train 1, including events with a reduction in LRV results for conductivity profiling. However during these events, a corresponding loss in LRV calculated using the traditional conductivity method was observed, with some results even reaching zero log for the traditional method. However, the data for these events revealed that these LRV results were in response to reductions in feed conductivity, as opposed to damaged vessels or membranes. While both methods showed sensitivity to this change, the conductivity profiling method remained above 2.0-log even with the reduced feed conductivity.

Train 3 had the lowest average LRV over the ten year period but also had a minimum LRV much higher than was seen in the other trains at MGDP. However, the train was also found to have an almost constant skew alert in the second stage over the entirety of its reported profiles: of the 56 conductivity profiles provided for Train 3, 49 had skew reported in the second stage. In other trains at MGDP, the skew alert could be used as an early warning of an outlier vessel, as skew alerts occurred more frequently than compromise alerts. An early warning of a potential compromise could result in more frequent testing of vessels to locate the source faster, even on a single stage as opposed to the entire train. Because Train 3 had a consistent skew alert, such an alert is not currently possible for this train. The use of the traditional conductivity method of LRV calculation also identified events where the LRV reached zero, but no

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decrease in feed conductivity was found for those events, and no corresponding change in the conductivity profiling method was found, either. These events did usually have extremely high recorded combined permeate conductivity, higher values than could be supported by vessel or stage specific conductivity readings and likely can be attributed to instrument error.

Analysis of Train 4 indicated similar performance to the other three trains at MGDP using the conductivity profiling method. However, analysis of conductivity profiling data from individual stages showed that the second train often outperformed the first; the first stage had an average LRV of 4.23-log while the second stage had an average of 4.32-log over the ten year period. While this is a relatively small difference, this behavior was not observed in the other three trains at MGDP, and no reason for the difference could be found in the data provided.

The alert conditions set forth by Vickers et al were found to be satisfactory for MGDP, apart from the skew alert in Train 3, and the alerts typically coincided with reductions in LRV credits for the stage where the alert occurred. These alerts serve as notifications of outlier vessels and where a potential defect capable of pathogen passage could be. A singular alert can serve as a notification that a breach exists and two alerts would serve as an alarm that such a breach is likely. Outlier vessels as determined by the standard deviation rule and the median rule, as set forth in Section 2.3.2.4, would be tested more thoroughly to determine the location of a faulty membrane or connection within the vessel itself. Sensitivity analysis, which would be done by using past conductivity profiling data combined with records of membrane repairs and replacement, would still be required to determine the best alert conditions for each train at MGDP.

A summary of alert events for MGDP can be found in Figure 4-3; there were more skew alerts than compromise events, suggesting that it could be an early indication of performance loss for this location. This is, of course, not the case for Train 3, where skew was a relatively consistent in the second stage. As expected, the number of alerts was greater for the second stage, which has a more concentrated feed than the first stage. There were relatively few instances where both stages had alerts, though such events did happen.
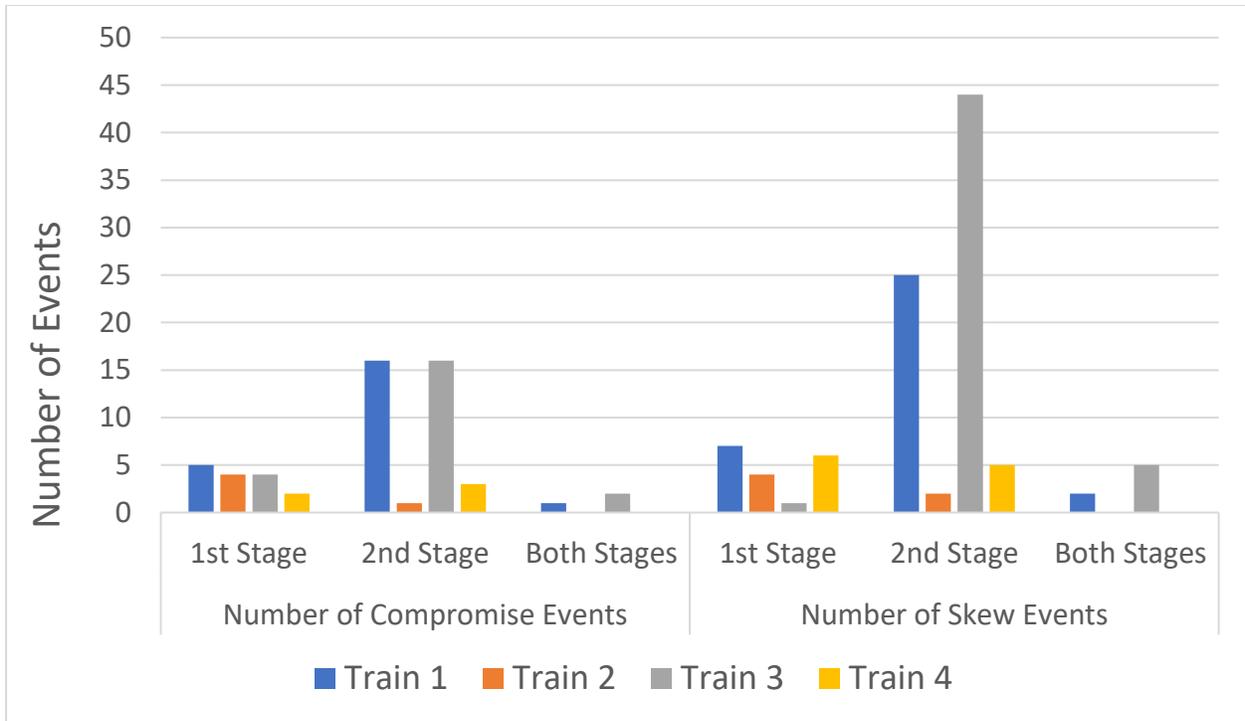
Figure 4-3: Summary of Alert Events for MGDP

4.2.2 Terminal Island Water Reclamation Plant (TIWRP)

For the second set of data, RO train profile data was provided by Terminal Island Water Reclamation Plant (TIWRP) in Los Angeles, California. TIWRP treats approximately 15 million gallons of wastewater from a mixture of industrial and residential sites in the Los Angeles area. The Advanced Water Purification Facility (AWPF) produces extensively treated, high-quality water for potable water replacement and blended water for industrial, environmental, and aquifer recharge purposes [89]. TIWRP currently has four RO trains in production treating microfiltration effluent; each of the four trains is able to produce approximately 3.0 million gallons of treated water per day at a typical recovery rate of 85%. Trains RO-A and RO-B have data dating back to January 2014 and trains RO-C and RO-D have data beginning in early to mid-2018.

TIWRP also saw a substantial increase in the LRV calculated using the conductivity profiling method as opposed to the traditional conductivity method of calculation, as shown in Figure 4-4 below. While only a single train (RO-B) was able to achieve a 5.0-log removal across its operational lifetime, all four trains had an average LRV above 2.5-log. There was not a noticeable difference in performance between older trains (RO-A and RO-B) when compared to a more recently installed train (RO-D); RO-C had the lowest performance of all four trains, with a minimum LRV comparable to the traditional conductivity method of LRV calculation. The trains at TIWRP also had less variability in train

performance than was seen at MGDP, even the trains that had been in operation for longer periods of time. Comparisons of the LRVs for the individual trains can be found in Appendix A.
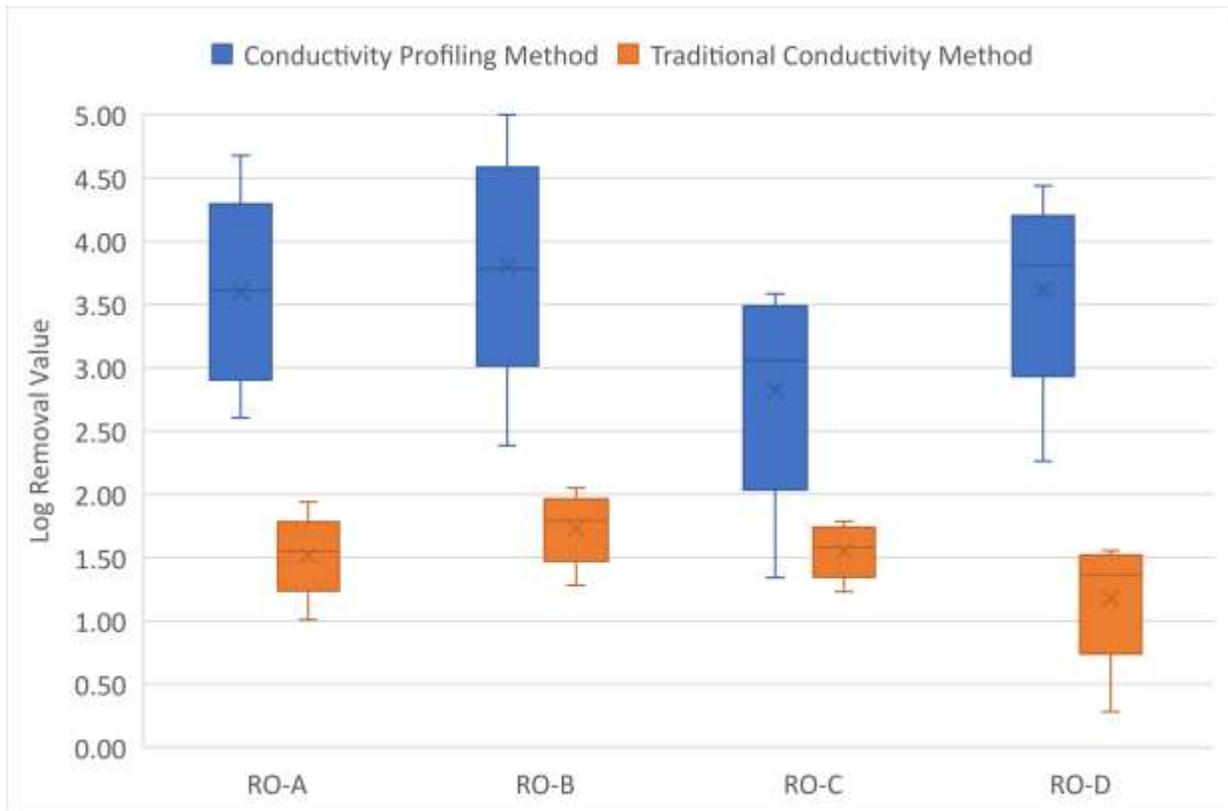

Figure 4-4: Average Log Removal Values for TIWRP

Analysis of the trains at TIWRP did have some issues, however. Several datasets had incomplete or missing flowrates, rendering analysis via the conductivity profiling method inaccurate or impossible. Statistical evaluation of the vessels could still be performed to determine outlier vessels, but a reliable LRV comparison for these datasets could not be performed. Data from RO-B and RO-C showed the sensitivity of both LRV calculation methods to changes in feed conductivity; one such event in RO-C resulted in an LRV calculated using the conductivity profiling method that was lower than that calculated using the traditional conductivity method due to a combination of reduced feed conductivity and an outlier vessel. Similar to MGDP, one of the trains analyzed was found to have better performance in the second stage as compared to the first. Analysis of RO-D returned frequent outlier vessel alerts on the first stage, with corresponding reduced LRVs, while the second stage remained at 5.0-log calculated removal.

The outlier vessel alert conditions were found to be less accurate for TIWRP, particularly for the more recently installed RO-C and RO-D. More compromise events were calculated than skew, meaning skew cannot be used as an early warning of an outlier vessel at this location. Additionally a majority of these alert events happened in the first stage as opposed to the second, particularly for compromise alerts

(based on standard deviation and exceeding the median, see Section 2.3.2.4 for more information). Based on this dataset, the removal of the median + 30% alert would likely be needed, as well as potentially a change in the standard deviation alert event, in order to accurately predict outlier vessels for this location.
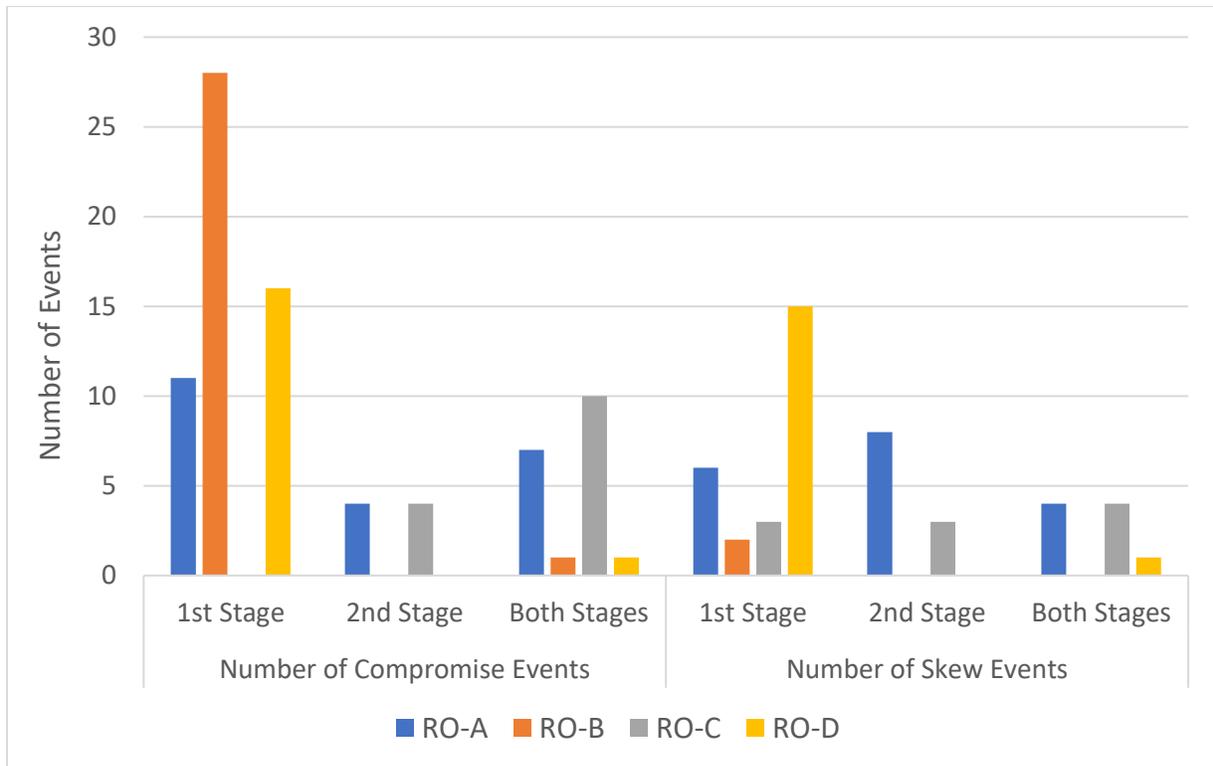

Figure 4-5: Summary of Alert Events for TIWRP

Apart from substantial breaches, the LRVs calculated using the conductivity profiling method were still above the credits granted by the traditional conductivity method of LRV calculation at both locations, supporting the idea that traditional conductivity calculations are unable to detect even large breaches in integrity. Indeed, a number of breaches identified through the traditional conductivity calculation method coincided with readings that were not supported by profile measurements, indicating that the lowered LRV was the result of conditions outside of the vessels themselves (i.e., conductivity equipment damage, errors in reporting, etc.).

The statistical rules set forth in Section 2.3.2.4 had greater accuracy for the relatively clean feed water at MGDP, which used groundwater as a source. TIWRP had more vessels per stage, but feed water had a higher conductivity because the facility had treated wastewater as a source. As can be seen in Figure 4-5 above, the first stage at TIWRP experienced more alert conditions for both compromise and skew, whereas MGDP had more alerts for skew than compromises. The conductivity profiling method is still applicable to both systems, and an early warning system is possible to implement at both locations

despite the differences in results. However, this early warning system of potential outlier vessels will be different between the two locations.

4.3 Application of selected molecular markers to a Closed Circuit Desalination (CCD) system

To evaluate several promising chemical markers for LRV calculations, experiments were conducted with the CCD system and two membranes, the NF-90 and the NF-270. Based on conductivity rejections, the NF-90 can be classified as a tight nanofilter while the NF-270 can be classified as a loose nanofilter. It is expected that the NF-270 will behave comparably to a compromised NF-90, which can, in turn, be considered comparable to a compromised RO membrane. The goal of the CCD experiments was to identify a marker capable of demonstrating large LRVs while being able to quantify the difference between membrane and integrity issues. The calculation of an LRV for the individual recoveries identified in Section 3.2 demonstrates the impact feed water concentration has on LRV calculation; these LRVs can be used as a guideline to determine what feed concentrations would be required to achieve high LRVs for the entire system.

As discussed in Section 3.2, samples were collected from the permeate, influent and concentrate streams at select recoveries and analyzed for the NF-270 and the NF-90 experiments. Graphs of marker concentration in the individual process streams (feed, permeate, concentrate) for the experiments are included in Appendix B. Average influent concentration for each marker is shown in Figure 4-6; the target concentration for the dosed markers (see Table 3-4) was not reached for either the NF-270 or NF-90 experiments. The dosing of sodium metabisulfite may have contributed to reduced measured concentration compared to the target concentration as certain solutes react with metabisulfite (a reducing agent), which may have decreased concentrations in the feed stream. Regardless, these feed concentrations allowed the assessment of LRVs using the studied chemical marker concentrations during operation of the CCD system.
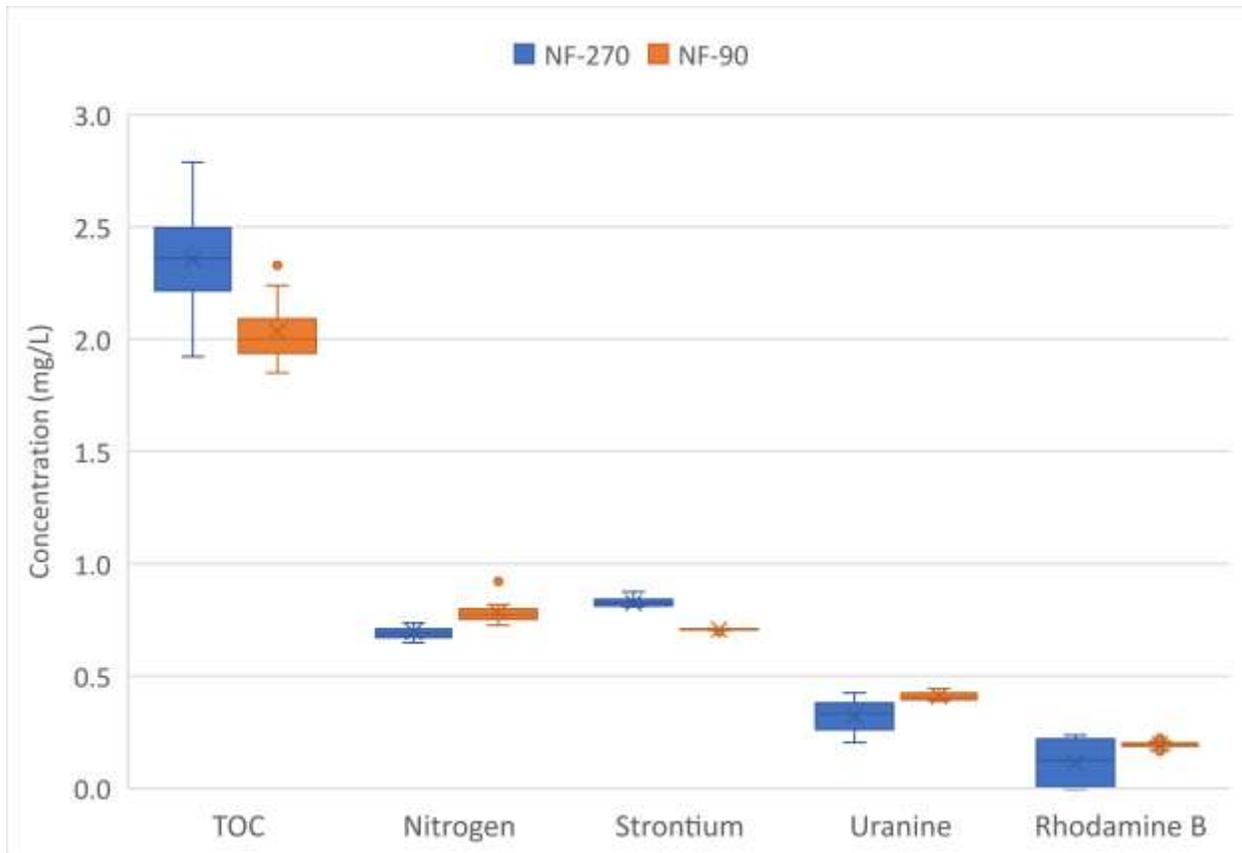
Figure 4-6: Average Influent Concentration of Tested Markers

Measured concentrations of the chemical markers in the combined permeate tank are presented in Figure 4-7. A discussion of the difference between samples collected from the permeate stream and the combined permeate tank can be found in Section 3.2. Analysis of chemical marker concentration in the combined permeate tank allows for comparison with marker concentrations collected from the permeate stream at the selected recoveries. Comparing marker concentration in the permeate stream at specific recoveries as opposed to in the combined permeate tank allows for an evaluation of the impact of recovery on marker passage through the membrane. If a marker is shown to have greater passage through a membrane at higher recoveries (when the recirculated concentrate is highly concentrated), the marker is likely not going to be able to fully demonstrate the removal capacity of an intact membrane at these recoveries.

Concentration of TOC in the combined permeate tank for the NF-270 experiment has been omitted as a statistical anomaly. Concentration of fluorescent markers in the NF-90 combined permeate tank is greater than that recorded from individual sampling points for the experiment, as well as the previous NF-270 experiment. Considering the difficulty in non-detects in the permeate stream samples, this may be a more accurate assessment of fluorescent concentration in the permeate.
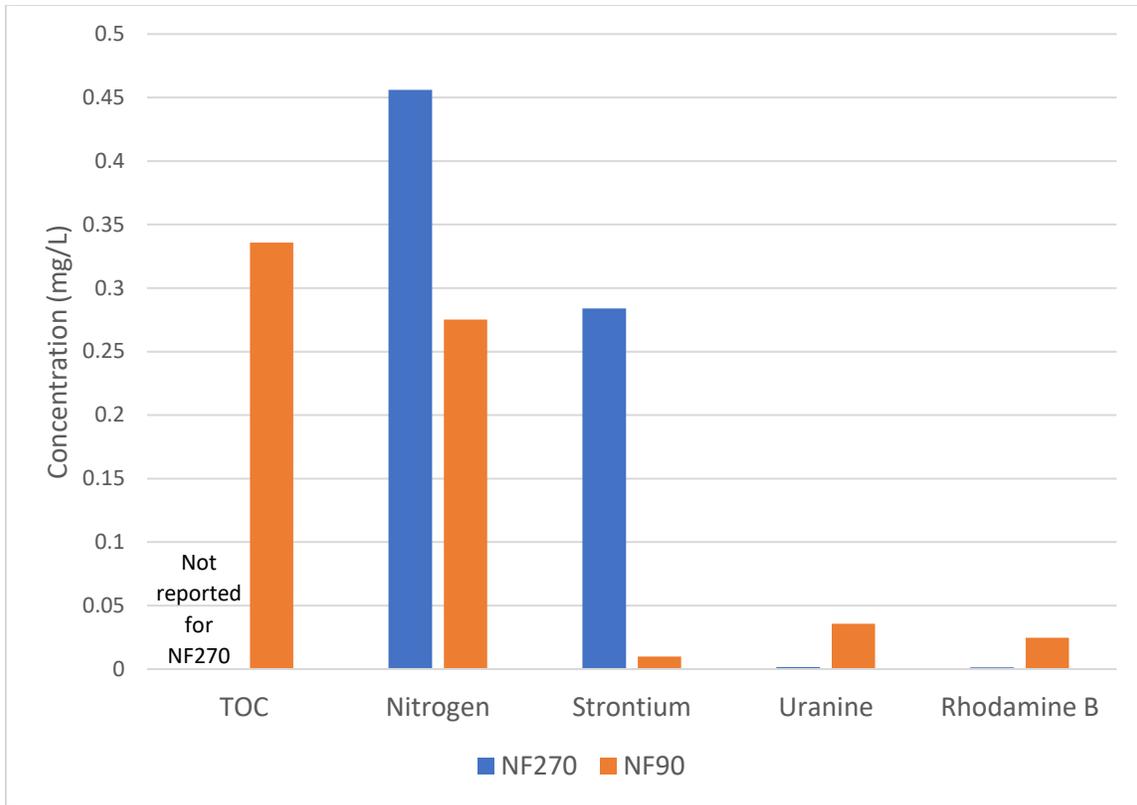
Figure 4-7: Marker Concentration in the Combined Permeate

LRVs calculated using average feed concentration and the concentration in samples collected from the combined permeate tank for the NF-270 and NF-90 membrane experiments were calculated using Eqn. 2.1 and are presented in Figure 4-8, below. It is worth noting that while LRV based on nitrogen and strontium were greater for the NF-90 membrane as compared to the NF-270 membrane, the opposite was true for the fluorescent markers. Considering the molecular weight for uranine and rhodamine B (376.28 g/mol and 479.02 g/mole, respectively) and the molecular weight cutoff of both NF membranes [85], an increase in LRV was expected for the fluorescent markers when comparing the NF-90 to the NF-270 due to the lower molecular weight cutoff of the NF-90. The lower LRV for the NF-90 as compared to the NF-270 means that it is unlikely to have an adequate LRV response to a compromised NF-90 membrane.

Strontium, however, was able to demonstrate an accurate difference in LRV between the NF-270 and NF-90 membrane. The NF-90 received an LRV almost 2.5-log greater than was achieved by the NF-270 based on samples collected from the combined permeate tank alone. This difference was substantial enough that a compromised NF-90 membrane could be easily detected using strontium as an integrity monitoring technique based on the lowered LRV. If a compromised NF-90 membrane were in use, it

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would behave similarly to an intact NF-270, and the LRV would be reduced enough that the compromise could be detected through regular strontium testing.
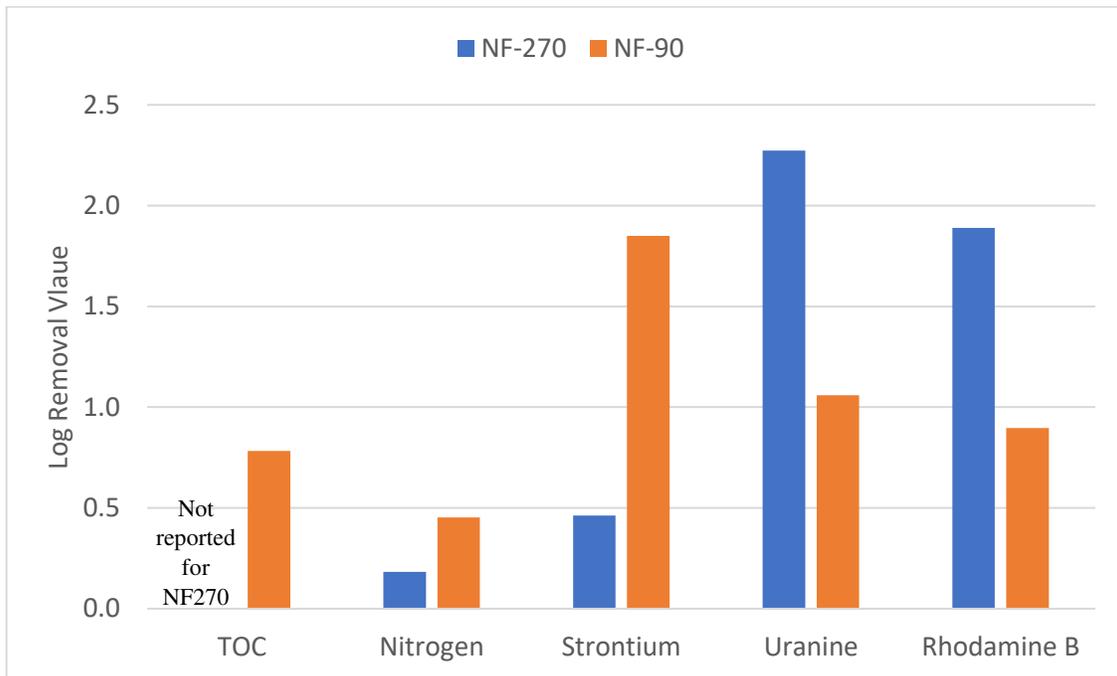

Figure 4-8: LRVs for each marker based on combined permeate concentration

The collection of CCD concentrate and permeate samples at selected recoveries (50%, 75%, etc.) allows for calculation of an LRV that includes the influence of recovery on increasing feed-concentrate concentrations, as discussed in Section 3.2. The graph of these LRVs for the NF-90 experiment is shown in Figure 4-9 below. Monitoring of strontium, which was able to differentiate the separation performance of the two NF membranes, is able to achieve even higher LRVs at the higher feed-concentrate concentrations measured at higher recoveries. However, once the system was above 90% recovery, there was little change in the LRV with increasing feed-concentrate concentration. Based on these values and Eqn. 3.5, the NF-90 would be able to achieve an LRV of approximately 3.25-log with a feed concentration of 6.0 mg/L. If the NF-90 were used in a CCD system at a feed concentration of 6.0 mg/L, the combined permeate would likely see a corresponding increase in LRV. While higher feed-concentrate concentrations could have increased LRVs due to the higher feed concentration, a substantial increase is not expected based on the LRVs shown in Figure 4-9.
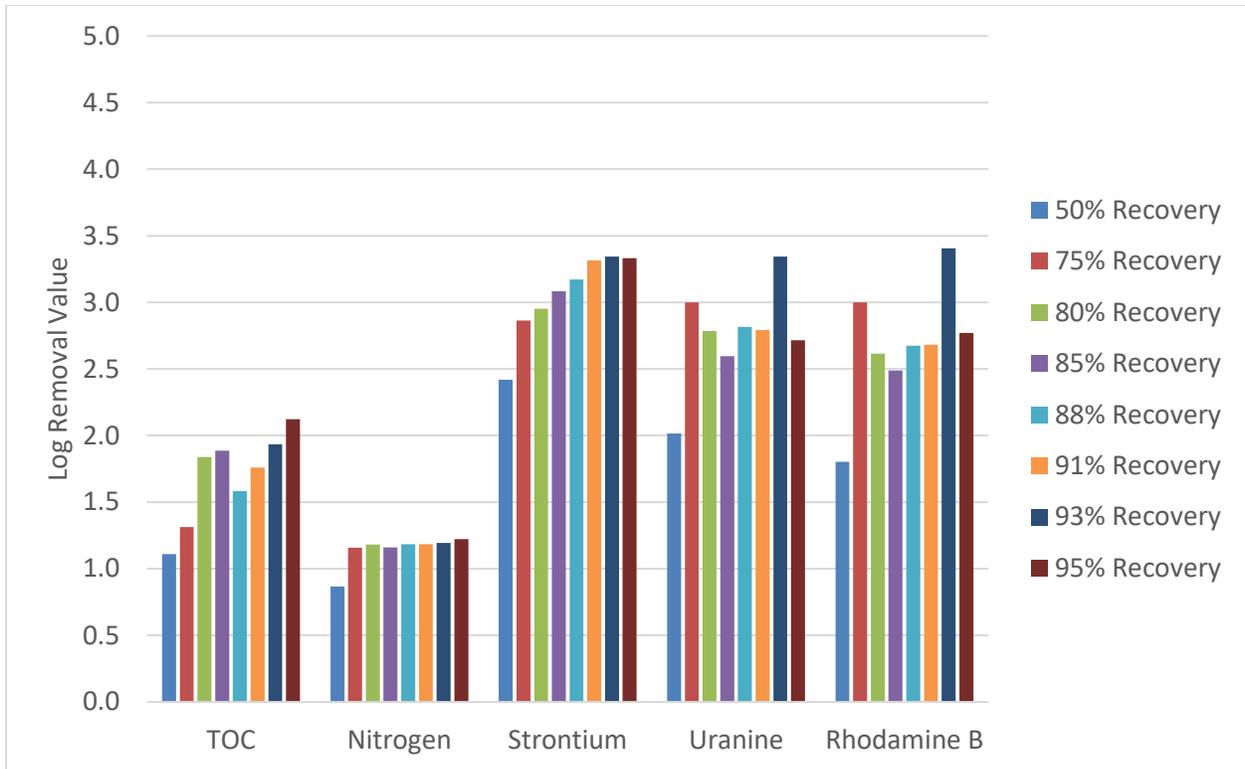
Figure 4-9: LRVs calculated for the NF-90 using recirculated feed-concentrate concentrations for selected recoveries

Sampling the feed-concentrate at recovery setpoints and the resulting increased concentrations of other markers did not show similar benefits as was seen with strontium. TOC, uranine, and rhodamine B had fluctuations in LRV when analyzed at different recoveries. This makes determining an ideal feed concentration to achieve a high LRV difficult, if not impossible. TOC is not expected to achieve above 2.5-log based on past studies of pilot and full-scale systems. Uranine and rhodamine B could be expected to be able to achieve an LRV of above 3.0-log at high concentrations based on the LRV calculated for 93% recovery, which correlates to an approximate feed concentration of 4 mg/L for uranine and 2 mg/L for rhodamine B. However, this was immediately followed be a sharp decrease in LRV calculated for the 95% recovery samples.

CHAPTER 5

CONCLUSION

The use of high pressure membranes in water treatment systems has become more common, particularly in the field of potable reuse, as facilities strive to produce high quality treated water. Regulations require water treatment utilities to regularly demonstrate the removal of harmful pathogens such as viruses, *Cryptosporidium* and *Giardia* through the calculation of LRVs for each treatment technology in use in order to protect human health. As water treatment regulations, particularly in the field of potable reuse, become stricter and more widespread in a bid to further protect human health, the accurate demonstration of the removal capacity of an intact high pressure membrane system becomes of vital importance. The MFGM was developed to provide facilities with validated approaches to monitoring the integrity of membrane systems and presents a method of calculating the LRV for individual technologies. However, obtaining LRVs that are indicative of true performance of high pressure membranes is difficult. The validated approaches in the MFGM are either inapplicable to high pressure membranes or do not have the resolution required to demonstrate the considerable removal capacity of high pressure membranes. The use of alternative markers is a challenge, both to obtain regulator acceptance and often on the actual implementation at the full scale. This research worked to identify promising integrity monitoring methods that would be applicable to large scale systems and meeting the requirements set forth by the MFGM. A comprehensive literature review was completed in order to identify methods that could be further evaluated through analysis or experimentation.

A significant amount of research has been performed on a wide variety of integrity monitoring approaches, from naturally occurring fluorescence and non-pathogenic virus particles to the addition of surrogate markers such as fluorescent dyes and nanoparticles. Because the goal of this research was to find markers that were sensitive to the performance of a membrane system and could realistically be implemented into the operations of a facility while fitting into the requirements set forth by the MFGM, the following markers were determined to be the most promising. The statistical analysis of conductivity profiling data would be perhaps the easiest to implement by a full scale facility, as conductivity profiles are already commonly collected, while demonstrating LRVs that correlated closely with the actual performance of a high pressure membrane systems. The fluorescent dyes uranine and rhodamine B were evaluated as they are one of the more realistic supplemental surrogate markers identified as part of the literature review. Strontium was evaluated as a potential naturally occurring surrogate marker due to the high LRVs previous studies have measured and its relatively high prevalence in wastewater streams.

The statistical analysis of conductivity profiles was evaluated using full scale facility data from two different water sources, groundwater and treated wastewater, to determine its wider applicability to

full scale systems. LRVs calculated using the statistical analysis method for both water sources were similar to the LRVs which an intact membrane system has been demonstrated to achieve. The combination of this method with alternative markers such as strontium or sulfate could further improve the demonstrated LRV. Additionally the statistical analysis method standardizes the identification of outlier vessels where defects may be present, reducing the downtime required to locate a defect. However while the statistical analysis method is based on principles introduced in the MFGM it does not easily fit within the regulations and would not be permitted as an integrity monitoring technique for high-pressure membrane systems.

Experimentation with the chemical markers for integrity monitoring of the CCD system demonstrated LRVs that were similar to previous research identified in the literature review. Use of strontium as a chemical marker resulted in calculated LRVs above 3-log for a tight nanofiltration (NF-90) membrane with high feed concentrations. These results indicate that strontium is a viable integrity monitoring method for high pressure membranes particularly for facilities with high feedwater strontium concentrations, which is common in wastewater streams. The use of fluorescent dyes, on the other hand, was far more problematic in practice. The calculated LRVs were lower for the NF-90 membrane experiment as opposed to the NF-270 membrane experiment, and LRVs calculated at individual recovery set points was highly variable. These results were unexpected because the tighter weave of the NF-90 membrane was predicted to have better rejection. Staining of the membrane elements, as well as the staining of the feed and concentrate tanks, make the use of fluorescent dyes challenging at the full scale. The use of a more practical or naturally occurring surrogate would likely improve acceptance by facilities and their operators.

The identification of an accurate yet practical integrity approaches is vital to obtaining credits that are representative of the performance of a high pressure membrane system. Statistical analysis of already collected conductivity data presents an opportunity to expand the way integrity is monitored without adding new costs to facilities that currently use high pressure membranes. The use of naturally occurring surrogates such as strontium are a monitoring method that more easily fits within the regulations but are limited to conservative LRVs. These methods represent relatively practical ways for full scale facilities to implement integrity monitoring and demonstrate LRVs that make the use of high pressure membranes a realistic option for water treatment.

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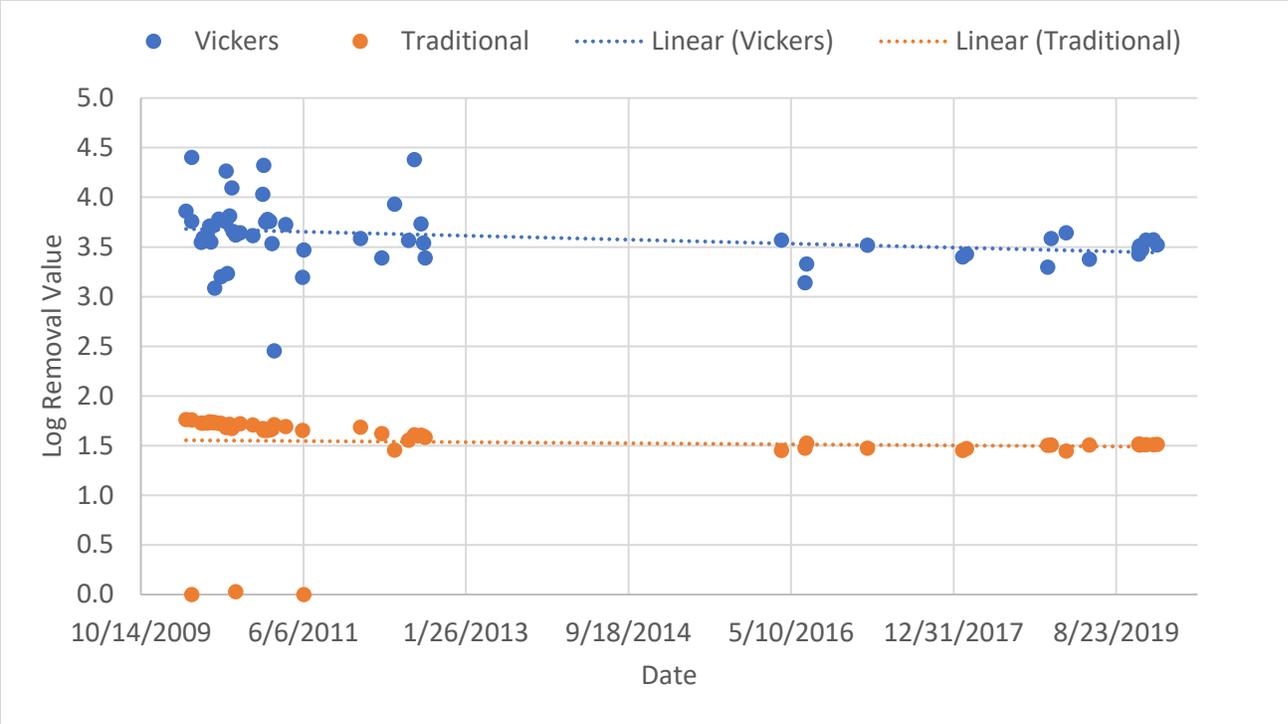   wwd-cw-p-tiwrp?_adf.ctrl-state=zazur7v9b_5&_afrLoop=6258985579489826#

Figure A-1: LRV Calculations for Mocho Groundwater Demineralization Plant, Train 1

Figure A-2: LRV Calculations for Mocho Groundwater Demineralization Plant, Train 2

Figure A-3: LRV Calculations for Mocho Groundwater Demineralization Plant, Train 3

Figure A-4: LRV Calculations for Mocho Groundwater Demineralization Plant, Train 4

Figure A-5: LRV Calculations for Terminal Island Water Reclamation District, RO-A

Figure A-6: LRV Calculations for Terminal Island Water Reclamation District, RO-B

Figure A-7: LRV Calculations for Terminal Island Water Reclamation District, RO-C

Figure A-8: LRV Calculations for Terminal Island Water Reclamation District, RO-D

INDIVIDUAL MARKER CONCENTRATIONS IN CCD EXPERIMENT STEAMS

Figure B-1: NF-270 Marker Concentration in the Influent Stream: 1st experiment (top)
and 2nd experiment (bottom)

Figure B-2: NF-270 Marker Concentration in the permeate stream: 1st experiment (top) and 2nd experiment (bottom)

Figure B-3: NF-270 Marker Concentration in the concentrate stream: 1st experiment (top) and 2nd experiment (bottom)
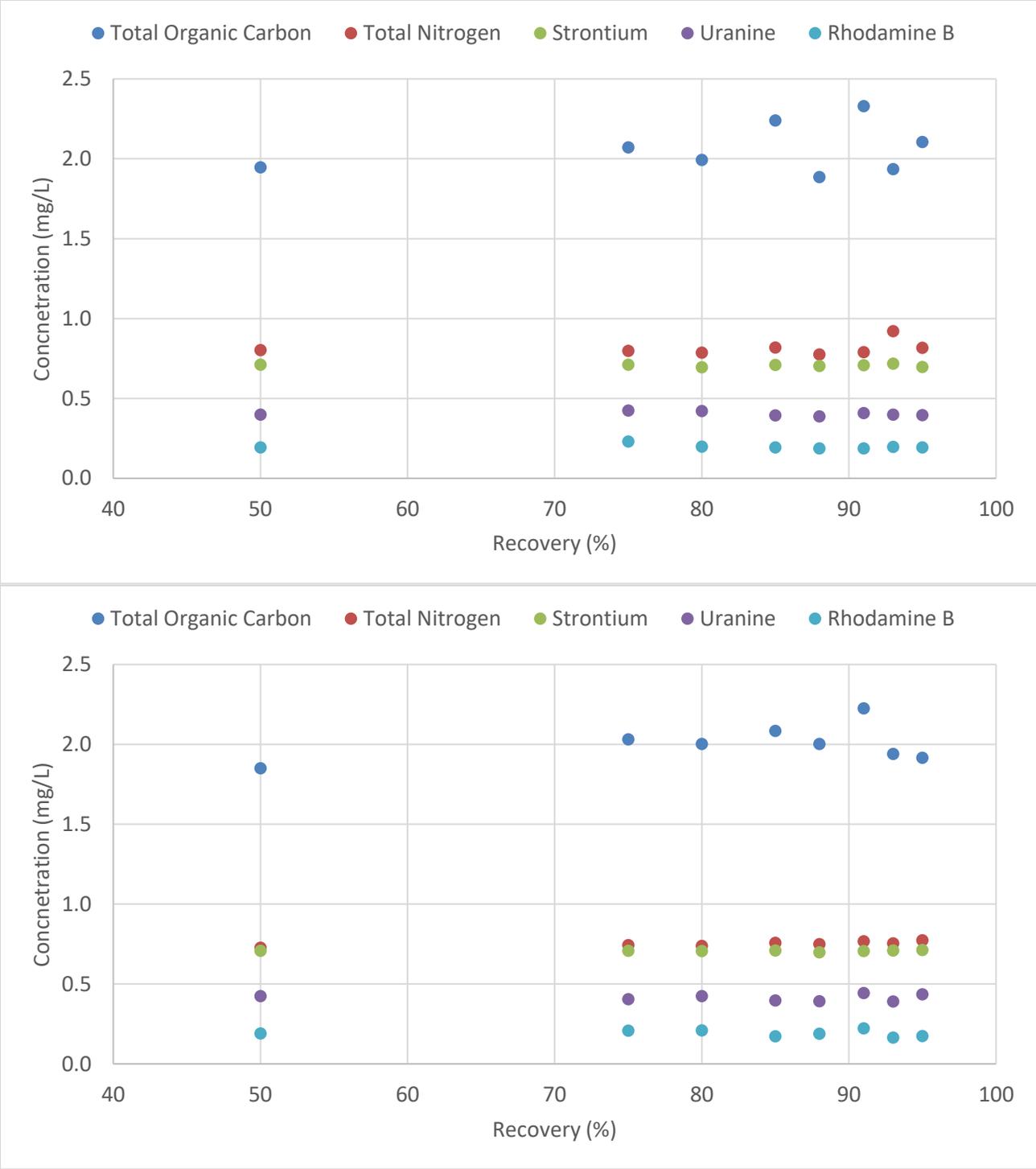
Figure B-4: NF-90 Marker Concentration in the Influent Stream: 1st experiment (top) and 2nd experiment (bottom)
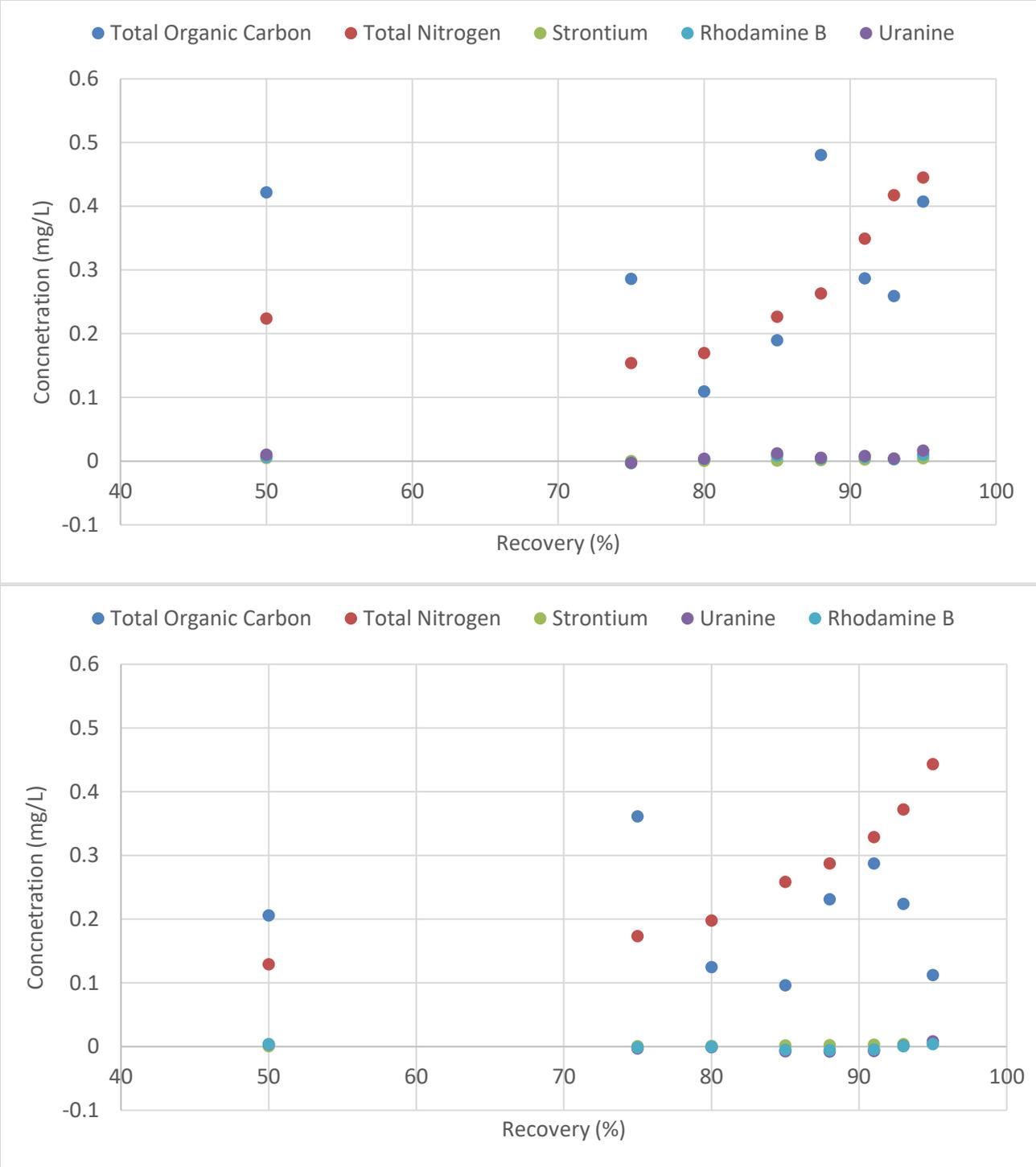
Figure B-5: NF-90 Marker Concentration in the Permeate Stream: 1st experiment (top)
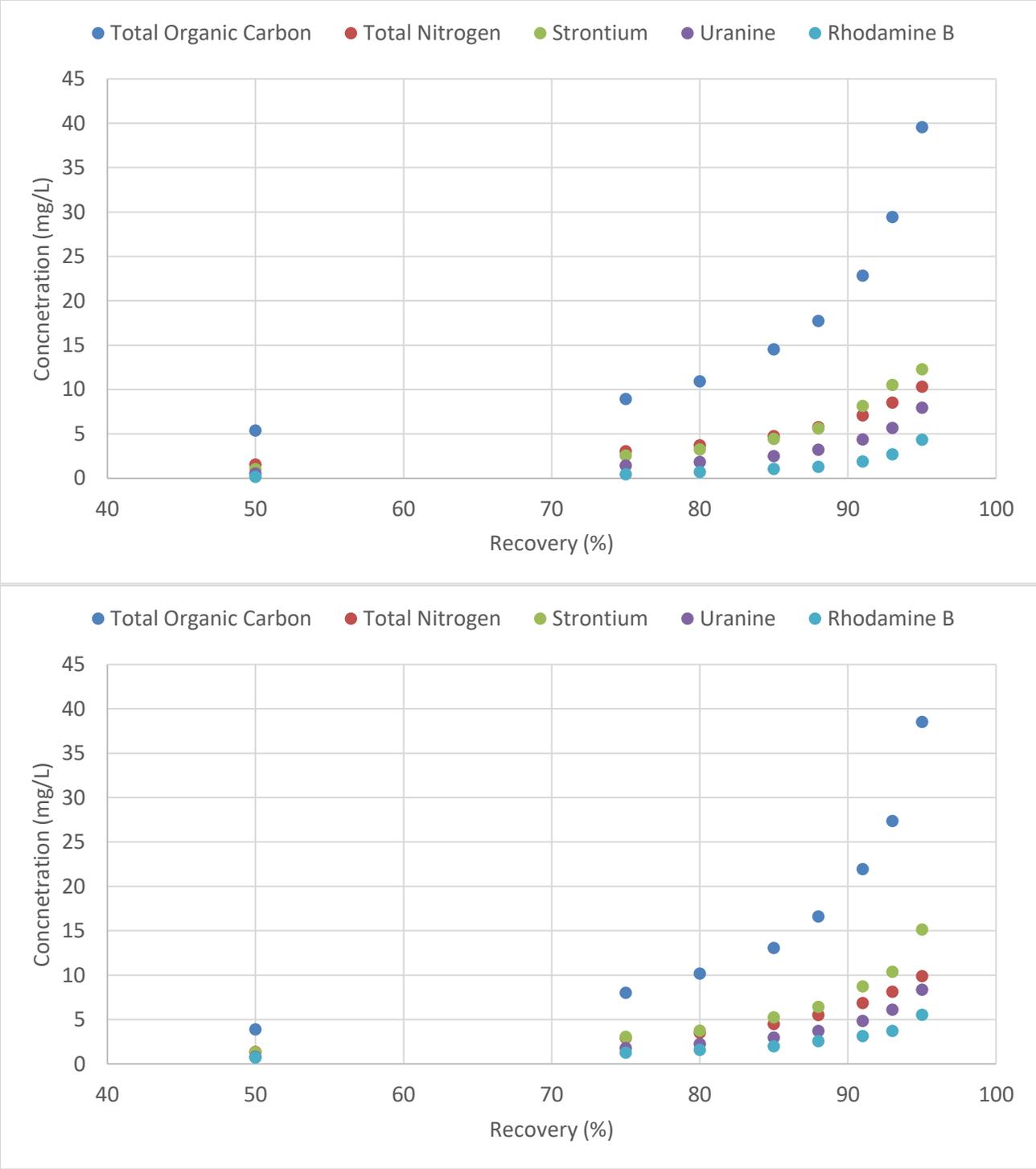and 2nd experiment (bottom)

Figure B-6: NF-90 Marker Concentration in the Concentrate Stream: 1st experiment (top) and 2nd experiment (bottom)

APPENDIX C

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