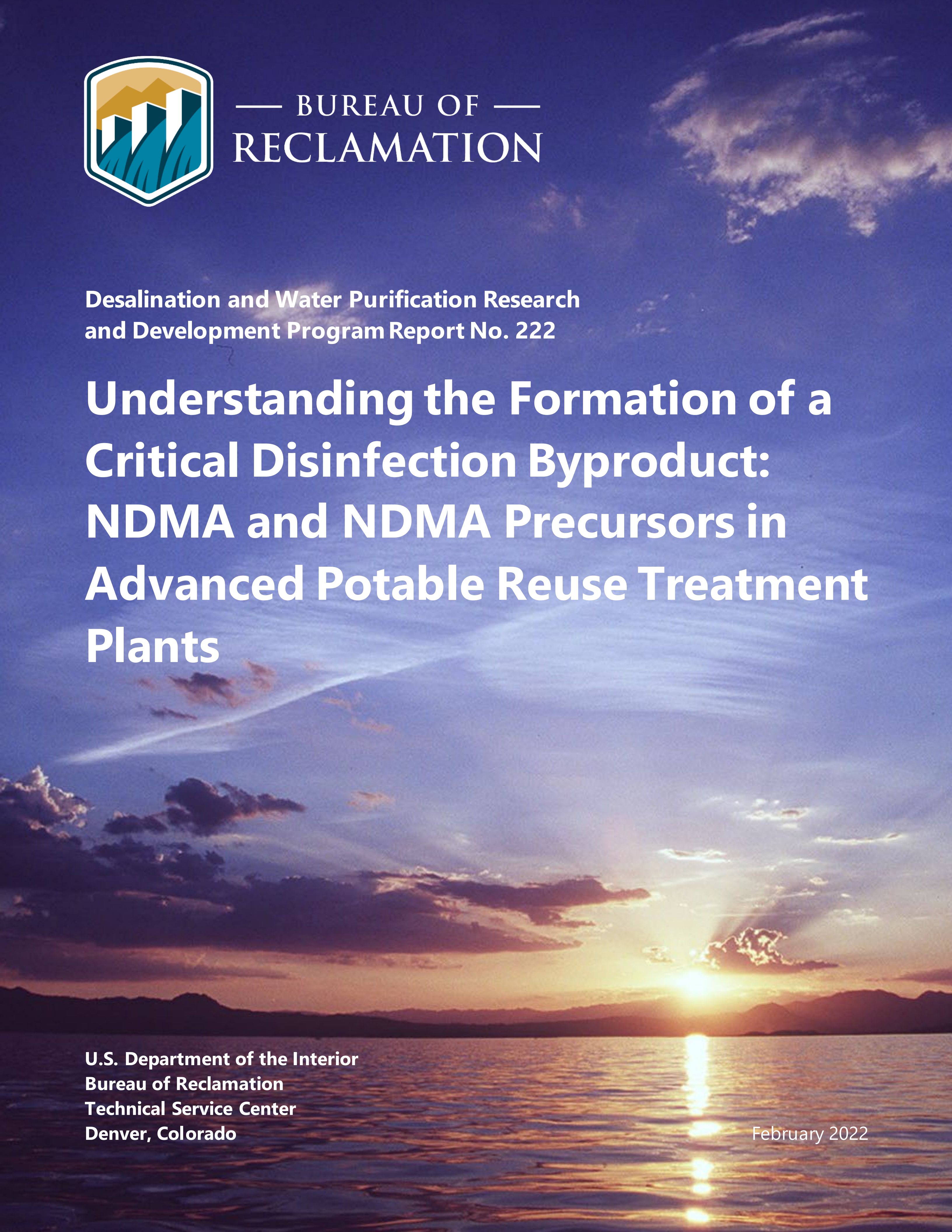

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Understanding the Formation of a Critical Disinfection Byproduct: NDMA and NDMA Precursors in Advanced Potable Reuse Treatment Plants

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14. ABSTRACT

Given the importance of *N*-nitrosodimethylamine (NDMA) as a disinfection byproduct of public health concern, and the industry interest in direct potable reuse, this study aimed to: 1) determine the occurrence and variability of both NDMA and NDMA precursors in an advanced water purification facility (AWPF) producing water for potable reuse, 2) assess the efficacy of reverse osmosis (RO) treatment for removal of NDMA precursors and the impact of membrane cleaning on rejection, 3) determine whether treatment chemicals added to the water during the purification process could be adding NDMA or other *N*-nitrosamine precursors, and 4) determine the efficacy of ultraviolet-advanced oxidation process (UV-AOP) utilizing different oxidants for the removal of NDMA, NDMA precursors, and trace organic compounds using non-target analyses. NDMA and NDMA precursor concentrations were variable over the course of the day and week in water samples from AWPFs. RO remained the clear primary contributor to overall NDMA precursor removal at the AWPFs which averaged 97.3 to 99.3 percent. RO membrane cleaning did not have a significant impact on the rejection of NDMA precursors, indicating that membrane cleaning damage is likely very minor or insignificant with respect to NDMA precursors. Chemicals added to the OCWD AWPF, such as antiscalant, acid, lime, polymer, and membrane cleaning solutions were not found to contribute additional *N*-nitrosamine precursors to the water and thus were not significant contributors to total formed *N*-nitrosamines at the plant. Efficacy of UV-AOP with different tested oxidants (pilot scale UV/H_2O_2, UV/HOCl, UV/supplemental NH_2Cl, and UV/residual NH_2Cl) for removal of NDMA precursors was variable between repeated events (i.e., precursors were removed to below detection limit in first pilot test event but showed no significant removal in the second test event), which can be attributed to the variability of the NDMA precursor pool coupled with very low UV-AOP feed concentrations of precursors. Based on the total number of compounds detected/qualified by non-target analysis, many compounds were removed by UV-AOP, and some unique transformation products were formed, for all four oxidant scenarios. Overall, non-target analysis was demonstrated to be a powerful tool for assessing the water quality polishing performance of UV-AOP. For example, LC-qTOF/MS revealed that greater than 98 percent of the total compound peak area (which is related to concentration) was removed by UV/H_2O_2 and UV/HOCl while only 61 to 65 percent was removed by UV/NH_2Cl (for supplemental or residual NH_2Cl).

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Understanding the Formation of a Critical Disinfection Byproduct: NDMA and NDMA Precursors in Advanced Potable Reuse Treatment Plants

Prepared for the Bureau of Reclamation Under Agreement Number R17AC00142

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Acronyms and Abbreviations

Acronym or Abbreviation	Definition
AWPF	Advanced Water Purification Facility
BCAA	Bromochloroacetic Acid
BDCM	Bromodichloromethane
CEC	Constituent of Emerging Concern
CL	Chemiluminescence
DBCM	Dibromochloromethane
DBP	Disinfection Byproduct
DCAA	Dichloroacetic Acid
DL	Detection Limit
DPR	Direct Potable Reuse
DPW	Decarbonated Product Water
EC	Electrical Conductivity
EEM	Excitation Emission Matrix
EfOM	Effluent Organic Matter
EPA	Environmental Protection Agency
FAT	Full Advanced Treatment
FP	Formation Potential
FPW	Finished Product Water
GC	Gas Chromatography
GCxGC-TOF-MS	GC by GC Time-of-Flight-Mass Spectrometry
GWRS	Groundwater Replenishment System
H_2O_2	Hydrogen Peroxide
HOCl	Free Chlorine
HPLC	High Performance Liquid Chromatography
IPR	Indirect Potable Reuse
LC	Liquid Chromatography
LC/QTOF-MS	LC/Quadruple Time-of-Flight Mass Spectrometry
MCL	Maximum Contaminant Level
MF	Microfiltration
MFE	Microfiltration Effluent
MFF	Microfiltration Feed
MS	Mass Spectrometry

Acronym or Abbreviation	Definition
MS/MS	Tandem Mass Spectrometry
NaOCl	Sodium Hypochlorite
ND	Non-Detect
NDMA	N-Nitrosodimethylamine
NH_2Cl	Monochloramine
NRC	National Research Council
NTA	Non-Target Analysis
OCSD	Orange County Sanitation District
OCWD	Orange County Water District
PDMWD	Padre Dam Municipal Water District
PPCP	Pharmaceuticals and Personal Care Product
PR	Photochemical Reactor
Q1	Secondary Wastewater Plant Effluent
Reclamation	Bureau of Reclamation
RO	Reverse Osmosis
ROF	Reverse Osmosis Feed
ROP	Reverse Osmosis Permeate
SDSU	San Diego State University
SPE	Solid Phase Extraction
TBM	Tribromomethane
TCAA	Trichloroacetic Acid
TCM	Trichloromethane
THM	Trihalomethane
TOC	Total Organic Carbon
TOrC	Trace Organic Chemical
UCB	University of Colorado Boulder
UFC	Uniform Formation Conditions
UNR	University of Nevada, Reno
UV-AOP	Ultraviolet-Advanced Oxidation Process
UVF	UV-AOP Feed
UVP	UV-AOP Permeate

Measurements

Unit	Measurement
µg/L	microgram per liter
ppb	parts per billion
MGD	million gallons per day
MLD	million liters per day
ng/L	nanograms per liter
mg/L	milligrams per liter
UV_{254}	UV absorbance at 254 nanometers
µS/cm	microsiemens per centimeter

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Executive Summary

Recycled water for potable reuse may contain wastewater-derived compounds such as unregulated organics. Unregulated organics may include recently discovered “constituents of emerging concern” (CECs) at trace levels that are not well understood and are difficult to remove, monitor, and assess for risk. The sheer number and variety of potential CECs can make it difficult to design a monitoring program. However, the National Research Council (NRC) highlighted the importance of disinfection byproducts (DBPs), and *N*-nitrosodimethylamine (NDMA) in particular relative to other trace-level CECs and organics, because DBPs like NDMA occur in treated wastewaters at levels closest to levels of potential human health concern (NRC 2012).

The goal of this study was to determine the occurrence and fate of NDMA and NDMA precursors at an advanced wastewater reclamation facility. The Orange County Water District (OCWD) Advanced Water Purification Facility (AWPF) in Fountain Valley, California utilizes microfiltration (MF), reverse osmosis (RO), and an ultraviolet-advanced oxidation process (UV-AOP) to recycle municipal wastewater for indirect potable reuse. NDMA and unknown precursors are present in the secondary effluent that feeds the plant. RO partially removes the NDMA while the UV-AOP effectively reduces its concentration below the 2 ng/L detection limit. However, a significant concern is that NDMA can form in the product water after UV treatment (i.e., reappears), likely due to the incomplete removal of NDMA precursors during advanced treatment.

Given the importance of NDMA as a disinfection byproduct of public health concern, and the industry interest in direct potable reuse, this study aimed to: 1) determine the occurrence and variability of both NDMA and NDMA precursors in an advanced water treatment plant, 2) assess the efficacy of RO treatment for removal of NDMA precursors as well as the impact of membrane cleaning on rejection, 3) determine whether treatment chemicals added to the water during the purification process could be adding NDMA or other N-nitrosamine precursors, and 4) determine the efficacy of UV-AOP utilizing different oxidants for the removal of NDMA, NDMA precursors, and trace organic compounds using non-target analyses. Work was completed by the Research and Development Department of OCWD, the University of Nevada, Reno, the University of Colorado Boulder, and San Diego State University.

NDMA and NDMA precursor concentrations were shown to be highly variable and ranged in concentration over the course of the day and week in water samples from AWPFs. In general, NDMA was found to slightly decline on the weekends. Based on the large increase in frequency of NDMA samples measured in this study compared to typical weekly compliance monitoring, NDMA only exceeded the 10 ng/L Monitoring Trigger Level in the advanced purified, finished water on two occasions. The concentrations of other DBPs (trihalomethanes [THMs] and haloacetic acids [HAAs]) also varied but remained an order of magnitude lower than

Environmental Protection Agency (EPA) Maximum Contaminant Levels (MCLs) for drinking water.

RO remained the clear primary contributor to overall NDMA precursor removal at the AWPFs and averaged 97.3 to 99.3 percent. RO membrane cleaning did not have a significant impact on the rejection of NDMA precursors, indicating that membrane cleaning damage is likely very minor or insignificant with respect to NDMA precursors. This finding may be membrane-specific for different manufacturer's membranes.

Chemicals added to the OCWD plant, such as antiscalant, acid, lime, polymer, and membrane cleaning solutions, were not found to contribute additional *N*-nitrosamine precursors to the water and thus were not significant contributors to total formed *N*-nitrosamines at the plant.

As the final water quality polishing step for advanced purified recycled water, UV-AOP was evaluated in this study to better understand the impact of different advanced oxidation process (AOP) oxidants on the removal or formation of NDMA, NDMA precursors, and unidentified compounds. NDMA was found to be well removed (to below the detection limit) by both UV/hydrogen peroxide (H_2O_2) and UV/free chlorine (HOCl) in pilot tests. However, in two of four tests utilizing UV/HOCl, NDMA was not removed to below the detection limit. This phenomenon was also observed in previous pilot tests by the study team that utilized the UV/HOCl process. With respect to NDMA precursors, the efficacy of UV-AOP with the different tested oxidants was variable between repeated events (i.e., precursors were removed to below detection limit in first pilot test event but showed no significant removal in the second test event). This can be attributed to the variability of the NDMA precursor pool coupled with very low UV-AOP feed concentrations of precursors.

During the same UV-AOP pilot tests, two methodologies for identifying non-target analytes were utilized in order to compare UV-AOP efficacy for a broad range of compound types (unidentified organics). These methodologies were applied to samples collected before and after UV-AOPs utilizing different oxidants. Based on the total number of compounds detected/qualified by non-target analysis, many compounds were removed by UV-AOP – and some unique transformation products were formed – for all four oxidant scenarios (UV/H_2O_2, UV/HOCl, UV/supplemental NH_2Cl, and UV/residual NH_2Cl). Compounds with both hydrophilic and hydrophobic character were removed and formed. More compounds were removed by UV/H_2O_2 and UV/HOCl compared to UV/NH_2Cl (both supplemental and residual NH_2Cl). Overall, non-target analysis was demonstrated to be a powerful tool for assessing the water quality polishing performance of UV-AOP. For example, LC-qTOF/MS revealed that greater than 98 percent of the total compound peak area (which is related to concentration) was removed by UV/H_2O_2 and UV/HOCl, while only 61 to 65 percent was removed by UV/NH_2Cl (for supplemental or residual NH_2Cl). The oxidant addition step, i.e., H_2O_2 or HOCl addition *prior* to treatment within the UV reactor, was found to remove compounds and form some byproducts as well, indicating that addition of the oxidant prior to UV-AOP influences the efficacy of the overall AOP system.

The overall conclusions of the study also include the following:

- Based on the high-frequency NDMA sampling conducted at AWPFs in this study, online NDMA monitoring may provide value to AWPFs if utilities can justify the cost in terms of benefits. Online NDMA instrumentation is not yet commercially available but has been developed in recent research studies. Utilities may elect to perform online NDMA monitoring if it provides operational value, public perception benefits, or aids in meeting regulatory requirements.
- NDMA remains a key water quality concern for potable reuse and its “rebound” (reappearance) in the finished water from AWPFs is due to the incomplete removal of NDMA precursors during AWPF treatment. In this study and other recent work, the OCWD AWPF achieves greater than 90 to 95 percent rejection of NDMA precursors by RO and more variable removal of NDMA precursors by UV-AOP (less than 10 percent to 100 percent). While future work may optimize UV-AOP to more consistently remove NDMA precursors, these results and other recent research by the study team indicate that no oxidant is clearly superior (comparing H_2O_2, HOCl, and NH_2Cl) for removing NDMA precursors, allowing utilities to use other criteria to select the AOP oxidant that is preferable for their treatment facility.
- There was no discernable or significant negative impact of RO membrane cleaning, or the use of AWPF treatment plant chemicals, on the occurrence or removal of NDMA precursors.
- Based on the use of non-target analysis to evaluate UV-AOP, UV-AOP removed more compounds than it formed. Non-target analysis proved valuable for comparing AOP oxidants beyond typical research focused solely on target compounds of interest.

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1 Introduction

The goal of this study was to evaluate the occurrence and fate of N-nitrosodimethylamine (NDMA) and NDMA precursors during advanced wastewater reclamation. Section 1 of this report provides the project background and describes the objectives of this study.

1.1 Project Background

As more utilities implement or consider potable reuse of advanced-treated wastewater to augment their drinking water supply, rigorous treatment and monitoring is essential for public health and safety (WHO 2017; Mosher et. al 2016). A major challenge to recycling water for this application is ensuring the effective removal of trace organic chemicals (TOrCs) which are found in wastewater and pose a threat to human health (Yu et al. 2015). TOrCs of concern include pharmaceuticals and personal care products (PPCPs), disinfection byproducts (DBPs), and industrial chemicals (Mosher et al. 2016; Yu et al. 2015). Reverse osmosis (RO) is used in advanced water treatment at potable reuse facilities to remove dissolved constituents like salts and TOrCs, as well as pathogenic bacteria and viruses (Roback et al. 2018a; Fujioka et al. 2013a; Fujioka et al. 2014). Most TOrCs, including pharmaceuticals and endocrine disrupting compounds, are removed by reverse osmosis. However, some TOrCs such as N-nitrosodimethylamine (NDMA) are known to readily permeate through RO membranes (WHO 2017; Fujioka et al. 2014; Sgroi et al. 2015).

The Orange County Water District (OCWD) Advanced Water Purification Facility (AWPF) in Fountain Valley, California was the primary study site for this project and utilizes microfiltration (MF), RO, and an ultraviolet-advanced oxidation process (UV-AOP) to recycle municipal wastewater for potable reuse via local groundwater recharge. NDMA and unknown precursors are present in the treated wastewater (secondary effluent) that feeds the plant. RO partially removes the NDMA while the UV-AOP effectively reduces its concentration below the 2 ng/L detection limit. However, a significant concern is that NDMA can form in the product water after UV treatment (i.e., NDMA reappears, or “rebounds”), likely due to the incomplete removal of NDMA precursors during advanced treatment. NDMA precursors are diverse and few are of known chemical composition.

1.2 *N*-Nitrosodimethylamine (NDMA) and Precursors

At concentrations that depend on the level of treatment, recycled water contains wastewater-derived compounds such as unregulated organics. Unregulated organics may include recently discovered “constituents of emerging concern” (CECs) at trace levels that are not well understood and are difficult to remove, monitor, and assess for risk. The sheer number and variety of potential CECs can make it difficult to design a monitoring program and assess risk. However, the National Research Council (NRC) recently highlighted the importance of disinfection byproducts (DBPs), and in particular NDMA, relative to other trace-level CECs and organics, because DBPs like NDMA occur in treated wastewaters at levels closest to levels of potential human health concern (NRC 2012). NDMA is one of a family of N-nitrosamines and is a DBP formed by the reaction of organic amine precursors with oxidants such as chloramines and ozone (Mitch et al. 2003; Krasner et al. 2013).

NDMA is listed as a contaminant of concern by the NRC due to its carcinogenicity at low concentrations and occurrence in treated wastewater at levels of perceived risk (Roback et al. 2018b). The Environmental Protection Agency (EPA) lists NDMA as a chemical of concern with a 10^{-6} lifetime excess cancer risk associated with human consumption at a 0.7 ng/L concentration in drinking water (EPA 1993). As a result, California's Department of Health Services set a drinking water notification level (NL) of 10 ng/L for NDMA, and the California Office of Environmental Health Hazard Assessment established a public health goal of 3 ng/L (CAEPA 2006). N-nitrosamines are currently under consideration for regulation in drinking water by the U.S. EPA (CAEPA 2006; McCurry et al. 2016). These drinking water standards are relevant to direct and indirect potable reuse. Recent studies have shown that wastewater effluents are a dominant source of N-nitrosamines including NDMA and NDMA precursors (Sgroi et al. 2018).

NDMA precursors can be pharmaceuticals, personal care products, water treatment polymers, and other anthropogenic chemicals (Krasner et al. 2013; Sgroi et al. 2018). NDMA is formed in chloraminated wastewater and wastewater-impacted water supplies (Krasner et al. 2013; McCurry et al. 2016; Sgroi et al. 2018; Krasner et al. 2009; Sedlak and Kavanaugh 2006; Mitch and Sedlak 2004). Organic NDMA precursors are known to be secondary, tertiary, and quaternary amines (Krasner et al. 2013). These precursors react with mono- and dichloramine to form NDMA and other N-nitrosamines (Mitch and Sedlak 2002). Of the proposed formation pathways, slow formation during chloramination of amines (i.e., precursor compounds to NDMA) is the most important. Studies indicate that wastewater is enriched in secondary and tertiary amines and effluent organic matter (EfOM) from wastewater contains NDMA precursors (Mitch and Sedlak 2004). However, the specific precursors responsible for the majority of the NDMA that forms as a DBP in treated wastewaters are unknown. Several studies have identified individual precursors in wastewater (Shen and Andrews 2011) but based on their low occurrence and typically low yields, the precursors identified to date cannot explain the levels of NDMA detected in treated wastewater. Hence, it is likely that a wide range of precursors, each occurring in low concentration, are together responsible for the measured NDMA concentration (Mitch and Sedlak 2004; Mitch and Sedlak 2002; Zeng and Mitch 2015).

RO is used by many advanced water treatment plants to remove or dramatically reduce the concentration of inorganics (e.g., salts, metals) and organic contaminants, but studies have shown that while RO effectively removes the vast majority of NDMA precursors, some precursors can remain (Sgroi et al. 2015). If NDMA precursors are not sufficiently removed by

RO or by a subsequent treatment step (typically UV-AOP in the United States), then the precursors are able to react with residual chloramines in the final product water and form measurable amounts of NDMA. As a result, NDMA has been detected post UV-AOP treatment despite complete removal of NDMA by the photolytic UV-AOP (Roback et al. 2018a; Sgroi et al. 2015). This occurrence, or rebound, of NDMA is a potential problem at water reuse facilities that must comply with permit requirements limiting the amount of NDMA produced in finished water or later in transmission lines. Control of NDMA formation is particularly necessary during treatment of wastewater-impacted water and potable reuse applications because one of the primary sources of NDMA precursors is treated wastewater (Sgroi et al. 2018). Thus, identifying the precursors responsible for NDMA rebound and improving their removal during water treatment is important for ensuring that regulations are met and maximizing the public health and safety of recycled water.

Studies show that NDMA passes through RO membranes largely due to its small size and uncharged nature, while many NDMA precursors are charged particles and more readily removed (Roback et al. 2018a; Chen et al. 2014; Fujioka et al. 2012). With respect to N-nitrosamines, the smallest N-nitrosamines (like NDMA) exhibit the lowest rejection (Fujioka et al. 2012). Thus, NDMA precursors that are not well-removed by RO treatment likely exhibit a smaller molecular size. As evaluated in the present study, it is possible that chemical cleaning of RO membranes may increase the passage of these small TOrCs due to a slight enlargement of the pore volumes and increased permeability (Fujioka et al. 2014; Al-Amoudi 2013).

Certain state regulatory agencies in the United States have mandated the application of an AOP as an additional treatment barrier for the removal of TOrCs that permeate through RO membranes during advanced treatment for potable reuse (Mosher et al 2016). AOPs can employ ultraviolet light with an oxidant, such as hydrogen peroxide (H_2O_2) or sodium hypochlorite, to produce highly reactive oxidative radicals that degrade NDMA and other TOrCs (Plumlee et al. 2008).

At its AWPF, the OCWD seeks to maintain NDMA concentrations less than the 10 ng/L NL in the finished product water from the facility. This recycled water is used to recharge a drinking water aquifer and meeting this objective helps ensure that the groundwater basin's water retailers will avoid exceedance of the California NL. Previous work by the project team showed that at the OCWD AWPF, UV-H_2O_2 AOP treatment inactivates or removes certain NDMA precursors and other TOrCs (Hokanson et al. 2019; Roback et al. 2017). Nevertheless, since NDMA precursors are not completely removed by the RO and UV/AOP treatment processes, NDMA can form at detectable levels in the transmission line delivering finished water (Roback et al. 2018a; Sgroi et al. 2015).

Various improvements in analytical methods have aided in the measurement of NDMA and NDMA precursors. Non-target analysis methods have recently been used to identify NDMA precursors present in reclaimed waters (Hanigan et al. 2017). Moreover, online or near-real-time methods of NDMA detection have been developed that have the potential to better inform treatment plant operators of changes in facility performance and water quality (Fujioka et al. 2017). A novel analytical method which uses high-performance liquid chromatography (HPLC), photochemical reaction (PR), and chemiluminescence (CL) has been developed for the fast and reliable determination of NDMA in water samples (Kodamatani et al. 2009; Roback et al. 2020; Kodamatani et al. 2016; Kodamatani et al. 2018; Fujioka et al. 2016). This system has the potential to be adapted into an online automated version capable of near-real-time detection of TOrCs in potable reuse water (Fujioka et al. 2017) and was utilized in the present study for plant monitoring.

1.2.1 Using Non-Target Analysis for Identifying NDMA Precursors

A non-target analysis (NTA) of a water sample is completed using mass spectrometry by screening for a large number of compounds and transformation products without a priori knowledge of the compounds present in the water (Roback et al. 2018b). NTA followed by targeted analysis are complementary approaches for evaluating the chemical composition of environmental samples (Mohler et al. 2013). Without an understanding of the specific identities of N-nitrosamine precursors present in raw water, it is difficult to design targeted methods and develop strategies to remove (treat) the precursors. NTA can be used as a first step to identify previously unknown compounds, which may include NDMA precursors, serving as a screening method for a large number of compounds and possible NDMA precursors present in water samples (Roback et al. 2018b).

High resolution time of flight mass spectrometry (TOF-MS) obtains a large amount of chemical information from a single analysis (Mohler et al. 2013), making it ideal for NTA. A recent study conducted by Hanigan et al. (2017) used NTA methods to isolate and identify potential NDMA precursors found in various wastewater samples and discovered 158 potential NDMA precursors. In this NTA study, wastewater samples were first processed by solid-phase extraction (SPE) and then analyzed by liquid chromatography/quadruple time-of-flight mass spectrometry (LC/QTOF-MS). Once a constituent of concern was tentatively identified using NTA, an analysis with chemical standards was conducted to confirm and quantify the concentration of the constituent by traditional methods of targeted mass spectrometry (MS), i.e., targeted analysis. A previous study used this NTA method to identify methadone, a commonly prescribed pharmaceutical drug, as an NDMA precursor (Hanigan et al. 2015). In this NTA method, LC/QTOF-MS is employed as a screening procedure to identify NDMA precursors present in wastewater followed by confirmation using tandem mass spectrometry (MS/MS). These studies demonstrate the benefits of NTA paired with targeted MS, which has the potential to improve water quality investigations.

An alternative method for target and non-target analysis consisting of two-dimensional gas chromatography columns coupled to time-of-flight mass spectrometry (GC×GC–TOF-MS) was optimized in a study conducted by Hoh et al. (2007) to maximize sensitivity and selectivity in the detection and separation of numerous compounds. In this study, GC×GC-TOF-MS was used in the analysis of 17 polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans, compounds which are toxic to human and environmental health. Comprehensive GCxGC employs two columns in tandem to separate individual analytes, which enables greater separation of the target compounds from the co-eluting matrix components. As a result, this method allows for the identification of a large number of compounds at low concentrations. Validation studies have been conducted through isolation by SPE and separation and characterization by GCxGC-TOF/MS (Hoh et al. 2008). Results showed that GC×GC-TOF-MS utilizes the faster spectral acquisition rates of TOF and increased chromatographic resolution of GC×GC to increase the sensitivity of the analysis and purity of the mass spectra (Hoh et al. 2007; Hoh et al. 2008). A similar study by Mohler et al. (2013) used GC×GC-TOF-MS to identify polar compounds in groundwater samples gathered from fuel release sites. GC×GC-TOF-MS was shown to be an effective tool to identify as many chemicals as possible in a water sample, allowing for potential identification of unknown compounds.

The study described in this report employed NTA to identify NDMA precursors and other trace organics utilizing both of the described methods, the LC/QTOF-MS method (Hanigan et al. 2017) and GC×GC-TOF-MS method (Hoh et al. 2008).

1.2.2 Impact of RO Membrane Cleaning on Removal of NDMA and NDMA Precursors

Although RO is a key treatment process in water reclamation applications for the effective removal of most TOrCs, NDMA rejection by RO membranes is highly variable (Roback et al. 2018a; Fujioka et al. 2012). Membrane fouling has previously been shown to negatively influence RO membrane performance (Ang et al. 2011) and increase the passage of small TOrCs such as NDMA (Fujioka et al. 2013). Chemical cleaning is employed by advanced water treatment plants to restore the performance of RO membranes exposed to wastewater foulants. However, recurrent membrane cleanings have been shown to damage RO membranes over time (Gabelich et al. 2005). Previous studies indicate that chemical cleaning may modify polyamide membrane structures, which increases permeability and in turn decreases rejection of small TOrCs (Fujioka et al. 2014). Results indicated that periodic chemical cleaning can potentially decrease the rejection of N-nitrosamines in full scale RO treatment plants.

The impact of chemical cleaning on the removal of TOrCs is more apparent for low molecular weight N-nitrosamines (Fujioka et al. 2014). Caustic chemical cleanings in particular have been shown to increase membrane permeability and cause a notable decrease in the rejection of N-nitrosamines (Fujioka et al. 2014). This effect may be due to a slight enlargement of the membrane pore volumes that occurs after chemical cleanings (Al-Amoudi 2013) and may result in an increase in the passage of NDMA and NDMA precursors through the RO membrane. A recent study by Roback et al. (2018) showed a decrease of 6 to 9 percent in NDMA rejection during the first four days after a cleaning event (Roback et al. 2018a). NDMA rejection returned to the pre-cleaning rejection rate after 11 days post-cleaning. However, the data observed in this study showed some variability in NDMA rejection throughout the day, possibly due to water quality changes that vary by the time of day. Hence, more work is needed to fully evaluate the influence of RO membrane cleaning on the passage of NDMA and NDMA precursors. This is the subject of the present study.

1.2.3 Online Monitoring of NDMA and Other TOrCs

Coupled with regular grab sampling of water treatment facilities, online water quality monitoring is an additional tool for improving plant operations and consumer confidence for advanced treated (recycled) water to ensure a robust monitoring program. Automated real-time monitoring via online sensors provides a vital diagnostic tool for process control during the advanced treatment of reclaimed waters (Yu et al. 2015). Online real-time analytical monitoring techniques or, alternatively, near-real-time analytical monitoring techniques, can indicate treatment failure and prompt corrective actions. Hence, online monitoring at continuous (i.e. instantaneous) or near-real-time (i.e., high frequency measurements) rates has the potential to improve safety and public confidence in finished water by providing operators with regular assessment of contaminant levels and early warnings of unforeseen contaminant spikes.

A novel analytical method first developed by Kodamatani et al. (2009) couples automated HPLC separation with PR and detection by CL as a method to measure N-nitrosamines in water in part-per-trillion concentrations. The HPLC-PR-CL method successfully detected N-nitrosamines in tap water, river water, and effluent from an industrial plant in Japan. Unlike conventional methods, the method requires no sample preparation (aside from filtration for samples with more complex matrices) and no sample concentration (via extraction); therefore, it can be used as a rapid screening method for N-nitrosamines in water samples. It also has the potential to be adapted for online NDMA analysis (Fujioka et al. 2018) due to its high speed, relative simplicity (no sample extraction/concentration), small required sample volumes, and high sensitivity. Moreover, the reduction of hazardous chemicals used in this method results in a “greener” and safer analytical method overall (Roback et al. 2020).

Recently, the HPLC-PR-CL method was evaluated for precision, accuracy, detection limits, and linearity using standard methods in a validation study by Roback and Plumlee (2019). These factors were assessed using criteria developed EPA Standard Method 521 for the analysis of N-nitrosamines (Munch and Bassett 2004). Split sample validation was also conducted by comparing the HPLC-PR-CL system with current commonly used analytical techniques. The split sample results indicate that the HPLC-PR-CL system demonstrates good performance relative to traditional NDMA analytical methods. Results showed that the detection limits of the HPLC-PR-CL system are similar to, or lower than, those of current N-nitrosamine analytical methods, and that accuracy and precision met EPA criteria. Validation of an online variation of the instrument was completed by continuously measuring concentrations of N-nitrosamines in an ultrafiltration-treated wastewater and RO permeate to track the variation in N-nitrosamine concentration as a function of changes in temperature and feed concentration (Fujioka et al. 2018). NDMA and other N-nitrosamine concentrations in ultrafilter-treated wastewaters were successfully monitored every 20 min for 24 hours and in RO permeate every 20 min over two days. These studies have shown that the HPLC-PR-CL system is a suitable method for N-nitrosamines analysis on par with conventional “benchtop” techniques and that it can be adapted for online or near-real-time monitoring.

1.2.4 Summary

Recycling water via advanced purification can provide a drought-resistant source of potable water for water-scarce regions and municipalities. Advances in treatment technologies such as RO and UV-AOP have improved the removal of trace organics from wastewater effluent and enabled producing potable water that meets drinking water guidelines. Novel analytical techniques including NTA and near-real time instrumentation may be utilized to better understand the water quality challenges posed by recycling water. N-nitrosamines, and NDMA in particular, are well removed by a combination of RO and UV-AOP to concentrations below detectable levels in the UV-AOP product water; however, due to a small number of NDMA precursors which are not fully removed and the presence of a residual chloramine disinfectant, NDMA can form after treatment in the finished water and in subsequent water delivery transmission lines, herein referred to as NDMA “rebound.” Minimizing NDMA rebound requires optimizing the removal of NDMA precursors (and if possible, minimizing the chloramine residual). With respect to the removal of precursors during advanced treatment, recent studies indicate that precursors are well removed – but not entirely – by RO and UV-AOP. Additionally, RO membrane cleaning can increase membrane pore sizes and/or degrade the separation layer and therefore increase the passage of NDMA and NDMA precursors.

1.3 Project Needs and Objectives

1.3.1 Needs

Current regulations for the safety of drinking water are applied to the finished product water produced by a given plant. For potable reuse treatment plants, permits specifying the regulatory requirements are developed for each plant based on state requirements. If an NDMA limit is specified in the permit, one sampling site is typically required, such as for OCWD’s AWPF. Therefore, many treatment plants do not regularly sample other locations within the plant for NDMA. With respect to sampling frequency, the permit will require periodic sampling, which is once per week in the OCWD case. Thus, there will be no information collected about diurnal NDMA variations.

As noted in Section 1.2.3, a new method for the analysis of NDMA has been developed that significantly reduces the required sample volume and eliminates the need for preparatory concentration prior to analysis. HPLC-PR-CL has the potential to be developed into an online monitoring system for use in indirect potable reuse (IPR) or direct potable reuse (DPR) advanced treatment facilities, addressing the need for greater understanding of occurrence and variability of NDMA.

With greater ease of monitoring, NDMA may be useful as a conservative surrogate for poorly-removed organic contaminants during processes such as RO treatment. If commercialized, an online monitoring tool could allow for treatment system benchmarking, continuous (high frequency) performance assessment, and collection of monitoring data for compliance with NDMA regulations. In a DPR scenario, the response time to react to process failure is critical for protecting public health. Water produced for DPR might be only a few hours away from delivery to people's homes, meaning traditional laboratory methods do not provide information with sufficient response time to confirm finished water quality. Thus, the capability to measure NDMA continuously would address the need for advances in online water quality monitoring for DPR. To the authors' knowledge, there is currently no available online analyzer that measures individual trace organic compounds aside from online sensors for trihalomethanes (THMs).

The present study also advances understanding of NDMA precursors. Knowledge of the organic nitrogen precursors of NDMA and the formation pathways is limited. Individual compounds at trace levels appear to contribute to the majority of the precursor loading, but researchers have yet to define the complete pool of NDMA precursors. Conventional wastewater treatment does not effectively remove NDMA precursors, so both treated and untreated wastewater have NDMA formation potential 10 to 100 times that of surface water, and surface waters with greater wastewater content form more NDMA upon chloramination (Krasner et al. 2013).

At OCWD, NDMA has been shown to increase in pipelines leaving the plant despite the reduction of NDMA to concentrations below the detection limit after UV-AOP treatment. The likely source of this NDMA reformation is the presence of NDMA precursors. These precursors may pass through RO membranes and may not be deactivated during UV-AOP treatment. The chloramine residual present in the finished product water reacts with the precursors that are still present to form NDMA. Therefore, a greater understanding of the type and quantity of NDMA precursors encountered in advanced water treatment plants is essential to the development of treatment techniques for the removal of precursors and reduction of NDMA formation during and after treatment.

1.3.2 Objectives

The overall goal of this study was to determine the occurrence and fate of NDMA and NDMA precursors during advanced water purification for potable reuse. Specific objectives of the study were to:

- Determine the usefulness of online NDMA monitoring as a tool for IPR/DPR facilities – i.e., whether there is a need for and benefit from investing in online NDMA analysis, alongside conventional analyzers such as electrical conductivity (EC) and total organic carbon (TOC).
- Measure the occurrence and removal of NDMA precursors at two AWPFs.
- Evaluate the potential impact of RO membrane cleaning on NDMA precursor rejection.

- Determine whether NDMA precursors are found in treatment plant chemicals (e.g., as impurities) used at AWPFs and if they could contribute to precursor occurrence at AWPFs.
- Compare different oxidants that may be used for UV-AOP with respect to the removal of NDMA precursors by UV-AOP.
- Evaluate non-target analysis using two different methodologies to explore the novel use of this tool for assessing UV-AOP treatment performance.

2 Technical Approach and Methods

This section describes the project facility, technical approach, and methods for each major research task.

2.1 Project Facility

The majority of sampling and experimentation for this project was completed at the OCWD AWPF in Fountain Valley, California. The AWPF produces high quality recycled water as part of the Groundwater Replenishment System (GWRS), a potable reuse project jointly operated by OCWD and the Orange County Sanitation District (OCSD). The GWRS is currently the world's largest water reclamation facility for indirect potable reuse and is a recognized industry standard. "Indirect" refers to the fact that the finished water is recharged into the groundwater aquifer (a drinking water source), as opposed to being used directly for drinking (delivery straight to tap). The facility uses full advanced treatment (FAT) to produce up to 100 million gallons per day (MGD) of potable quality water from secondary-treated wastewater. The AWPF treatment train is comprised of MF, RO, UV disinfection, and hydrogen peroxide addition, referred to as the UV/H_2O_2 AOP, followed by decarbonation and lime stabilization (Figure 1).

Some sampling was also completed at Padre Dam Municipal Water District (PDMWD) in Santee, California. PDMWD is currently operating a 100,000 gallon per day demonstration advanced water treatment facility to treat wastewater for future augmentation of a drinking water reservoir. The facility employs RO and UV-AOP, similar to the OCWD's AWPF; however, the AOP at this facility is comprised of UV/free chlorine (HOCl) treatment (Figure 2).

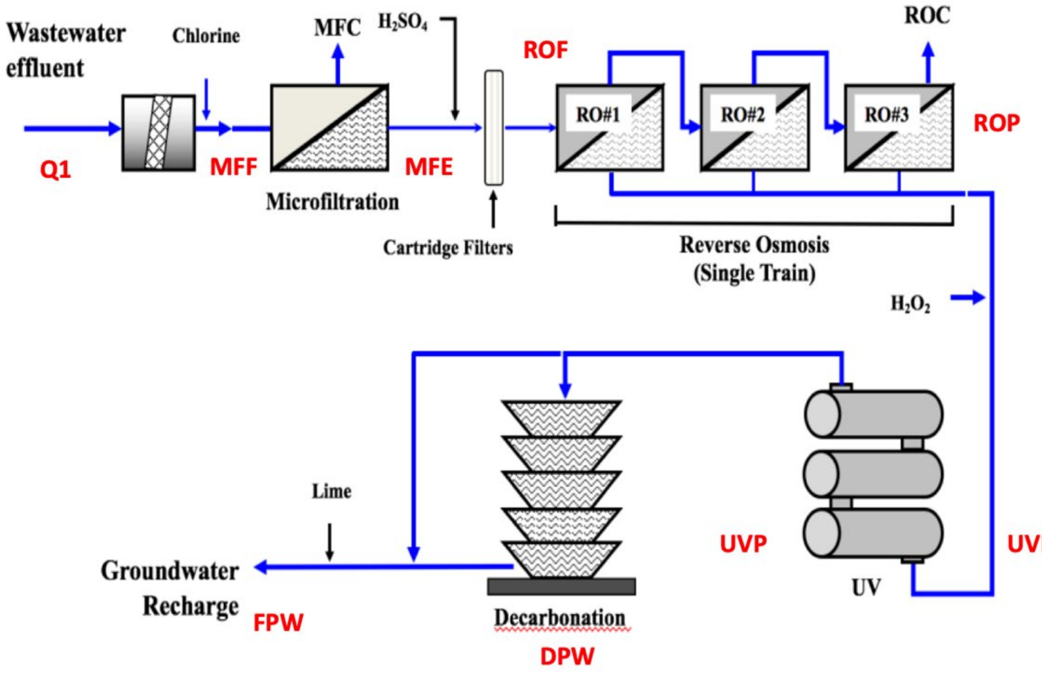


Figure 1. OCWD GWRS Advanced Water Purification Facility (AWPF) process flow diagram. NDMA and NDMA Precursor sampling locations from occurrence task (Section 3.2) indicated in red.

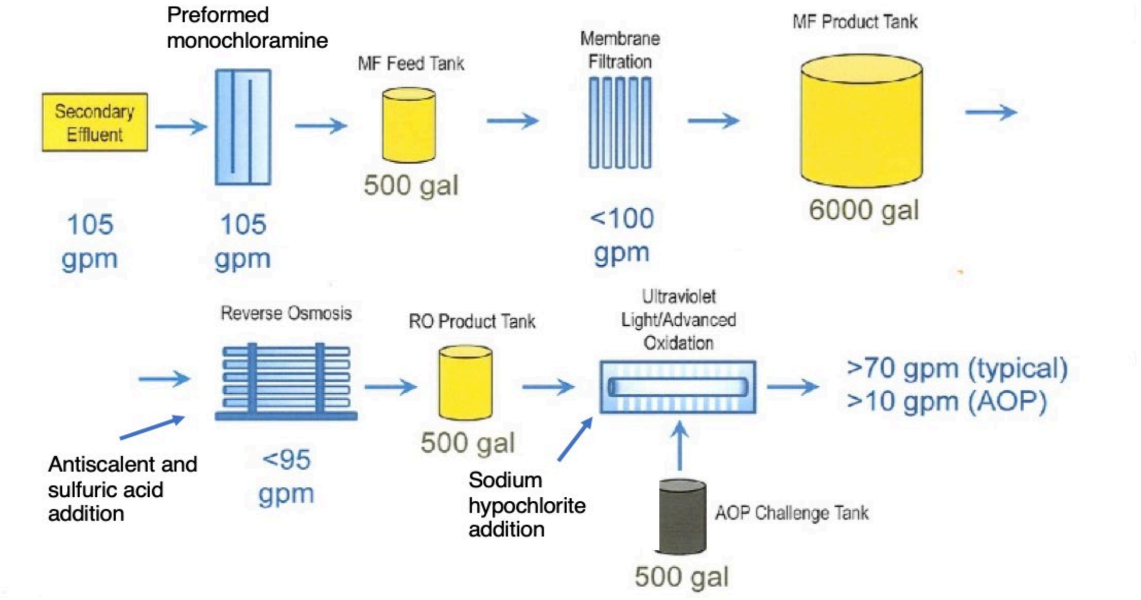


Figure 2. PDMWD Full Advanced Treatment Demonstration Project Plant schematic

2.2 High Frequency Monitoring of NDMA at AWPF

In order to demonstrate whether there is a benefit from and need for an online NDMA monitor, a large data set of high frequency NDMA measurements was collected. Contemporaneous samples were analyzed for other DBPs, electrical conductivity (EC), total chlorine, and emission excitation matrix (EEM) fluorescence spectra to determine if any of these water constituents are correlated with the occurrence of NDMA. Samples were collected from several different locations in the plant (before and after treatment steps) to establish trends and benchmark performance.

The purpose was to document the NDMA occurrence at a high frequency (e.g., multiple times per day) at multiple locations to reveal where an NDMA online monitor would have the most value for compliance or process control. Limited sampling was also completed at PDMWD for comparison of trends.

The very large number of NDMA samples collected for this study, far greater than any other single-facility drinking/wastewater study of NDMA in the literature, was made possible by the newly available HPLC-PR-CL NDMA analysis method that was employed in this study.

2.3 Evaluation of NDMA Precursor Occurrence

In order to assess the occurrence, addition, or removal of NDMA precursors through FAT, precursors were measured using a formation potential (FP) test at locations throughout the OCWD AWPF and PDMWD during summer, fall, and winter seasons. The FP test involves chloramination of the sample for a period of time (days) and measuring the resultant NDMA, such that the amount of NDMA formed serves as an indirect measure of the precursor load in the sample. This approach is commonly used (Krasner et al. 2013; Hanigan et al. 2015; Hoh et al. 2007; Chen and Westerhoff 2010; Hanigan et al. 2016) and is required because individual NDMA precursors cannot be measured directly since they are largely unknown. The fate of precursors through advanced treatment were assessed by measuring NDMA FP before and after various treatment processes at OCWD and PDMWD AWPFs.

2.4 Impact of Membrane Cleaning

RO membranes are periodically cleaned (approximately every six months to one year) to address membrane fouling and restore performance. Previous studies and plant operational experience has shown that this can lead to increased passage of salts and other compounds over time. RO is the primary barrier for the removal of NDMA precursors. However, the impact of membrane cleaning on the removal of NDMA precursors is unknown. Additionally, compounds used for membrane cleaning may contain unknown chemicals or contaminants that could be NDMA precursors. In previous work completed at OCWD (Roback et al. 2018b), non-targeted analysis revealed detergent-like NDMA precursors in the RO permeate but not in the RO feed, suggesting introduction of an NDMA precursor into the water matrix.

For this study, RO feed and permeate samples were collected at multiple time points before and after two full-scale membrane cleanings. NDMA and NDMA precursors (NDMA FP) were measured. Additionally, a survey of the percent rejection of NDMA and NDMA precursors from all membrane units in the facility was completed in order to better understand the typical rejection rate.

2.5 Contribution of NDMA to Treated Water from Plant Chemicals

To determine whether NDMA precursors are found in treatment plant chemicals (e.g., as impurities) used at AWPFs and in this way could contribute to precursor occurrence at AWPFs, OCWD plant chemicals were tested for occurrence of NDMA and NDMA precursors. The method for NDMA precursors (FP) testing is described in Section 2.3. Aliquots of eight chemicals added at different stages of the OCWD AWPF were shipped to University of Nevada, Reno (UNR) for NDMA and NDMA precursor analysis. Chemicals were shipped at concentrations and phases (i.e., solid, liquid) as received from vendors by OCWD and used at that facility.

2.6 Non-Target Analysis to Evaluate UV-AOP

Given that NDMA formation from precursors has been observed in advanced reuse facilities even after the UV-AOP treatment step, the objective of this research task was to evaluate the destruction of trace organics including NDMA precursors by the UV-AOP step for three different AOP oxidants. OCWD currently uses an H_2O_2-based AOP system, while other facilities (e.g., PDMWD) use different oxidants (e.g., HOCl and chloramines).

NTA was conducted using four different UV-AOP scenarios via pilot testing: (1) UV/H_2O_2, (2) UV/free chlorine (HOCl), (3) UV/supplemental monochloramine (NH_2Cl), and (4) UV/residual NH_2Cl. The fourth case refers to operation of the UV pilot with UV light only (no added oxidant), in which the UV pilot feed water (RO permeate) has a residual concentration of NH_2Cl related to upstream use of NH_2Cl in the plant for membrane biofouling control. The AWPF RO permeate (ROP) was used as the UV feed water for each of the four scenarios and each experiment was conducted twice (i.e., two UV-AOP pilot events on different dates, with each event featuring multiple oxidant scenarios) utilizing OCWD's pilot scale UV-AOP reactor that is designed and operated to simulate the full scale AWPF UV-AOP treatment system. NTA were conducted using two different non-target methodologies described below. The mass spectra from each sample were searched against spectral databases to make tentative compound identifications. Confirmation of compound identifications requires additional testing with authentic standards, which is an additional step of non-target analysis that was not completed in this study.

2.6.1 Non-Target Analysis by LC/qTOF-MS

The first non-target methodology consisted of solid phase extraction (SPE) followed by LC-qTOF/MS. The analysis was conducted at UNR and University of Colorado Boulder (UCB). An SPE method developed for the extraction of NDMA precursors was employed in the first event and an SPE method targeted to capture a wider variety of compound types was employed in the second event. The NDMA precursor extraction involves SPE at low pH to recover protonated amines with a cation exchange column. NDMA FP tests were conducted on the initial sample and an aliquot of the isolated precursors to determine the efficiency of the recovery. Previous published research indicated approximately 75 percent recovery of NDMA precursors from environmental samples (Hanigan et al. 2017), but lower recovery in AWPF samples (Roback et al. 2018b). The isolates (extracts) were then shipped to UCB for LC-qTOF/MS analysis. In the second event, Oasis HLB cartridges were used to capture a broader spectrum of compounds and were preconditioned with 10 mL methanol, followed by HPLC grade water. Aqueous samples were not pH adjusted and 1000 mL was loaded to the cartridge. The cartridge was dried and eluted with 10 mL methanol and reduced in volume to 1 mL. The concentration factor was 1,000-fold to avoid breakthrough of polar analytes on the HLB cartridge. Extracts were then shipped to UCB for LC-qTOF/MS analysis, as in the previous event.

Two qTOF methods were used to characterize the samples. The first method searched for over 100 pharmaceuticals and pesticides based on a proprietary database of retention times, isotope pattern spacing, and accurate masses. The second approach made use of the collision cell and searched for compounds that fragment to produce a neutral loss of 45.0578 u, the exact mass of the dimethylamine NDMA precursor moiety. By searching for compounds that produce this fragment, unknown NDMA precursors in complex matrices can be identified.

2.6.2 Non-Target Analysis by GC×GC/TOF-MS

The second non-target methodology consisted of SPE followed by GC×GC/TOF-MS. The analysis was conducted at San Diego State University (SDSU). Oasis HLB cartridges were used for SPE preconditioned with 5 mL of dichloromethane (DCM) followed by 5 mL of acetone, then 5 mL methanol and followed with 15 mL LC/MS grade water. Compared to the first non-target analysis SPE method (for NDMA precursors) from the first event (previous section), SPE with Oasis HLB is expected to be broader with respect to the chemical characteristics of compounds that would be captured. An automated tubular transfer system was used to load 1 L water samples to the SPE cartridges at a flow rate of 6 mL/min. Samples were eluted with 5 mL DCM followed by 5 mL acetone. Anhydrous sodium sulfate (5 g) was added to each extract to removal residual water. In addition, each extract was passed through UCT EnviroClean (6 mL, United Chemical Technologies, Inc., Bristol, Pennsylvania) glass cartridges loaded with 2500 mg muffled sodium sulfate for further drying. Finally, extracts were placed into a water bath at 40°C and concentrated to 400 µL under a stream of nitrogen.

The “Statistical Compare” add-in feature of LECO ChromaTOF instrument software was used as a complementary data mining tool for identification of statistical differences between groups of samples, e.g. UV-AOP feed and product water. True detection of a recovered compound was determined by meeting two criteria: it must be found in all duplicates, and it must be present at 5:1 ratio of peak area compared to any of the field blanks.

3 Results and Discussion

This section describes the results for the following major research tasks:

- High frequency monitoring of NDMA during advanced treatment (Section 3.1);
- NDMA precursor occurrence and fate in advanced treatment facilities (Section 3.2);
- Impact of membrane cleaning on NDMA and NDMA precursor removal (Section 3.3);
- Contribution of NDMA to treated water from treatment plant chemicals (Section 3.4); and
- Impact of UV-AOP scenarios on NDMA precursors and unidentified trace organics (Section 3.5).

3.1 High Frequency Monitoring of NDMA during Advanced Treatment

Multiple sampling events were completed at OCWD and PDMWD facilities to characterize variation of NDMA, NDMA precursors, and other constituents, as well as to evaluate the potential usefulness of online NDMA monitoring as a tool for IPR/DPR facilities. Sampling events in 2017 included both NDMA and NDMA precursors, while sampling events in 2019 included only NDMA with other constituents.

3.1.1 NDMA/Precursor Occurrence at OCWD AWPF (2017)

Two sampling events were completed prior to the commencement of the Reclamation-funded project in August and November of 2017 and are included in this report due to relevance. The sampling sites consisted of AWPF influent (which is secondary treated wastewater effluent prior to chlorination), RO permeate, and finished product water (which has been treated by UV-AOP and subsequent lime addition and partial decarbonation for corrosion control).

Sampling in August 2017 took place over six days (Tuesday to Sunday) and included monitoring for NDMA as well as NDMA precursors. Sampling for the same parameters in November 2017 took place over seven days. Results shown in Figure 3 and Figure 4 show that diurnal fluctuations exist for both NDMA and NDMA precursor concentrations. This variability is most pronounced in the plant influent water and the trend in variation propagates through RO treatment. It appears that almost all NDMA and NDMA precursors are removed in the final product water; therefore, there was less variation of concentration at this sampling location.

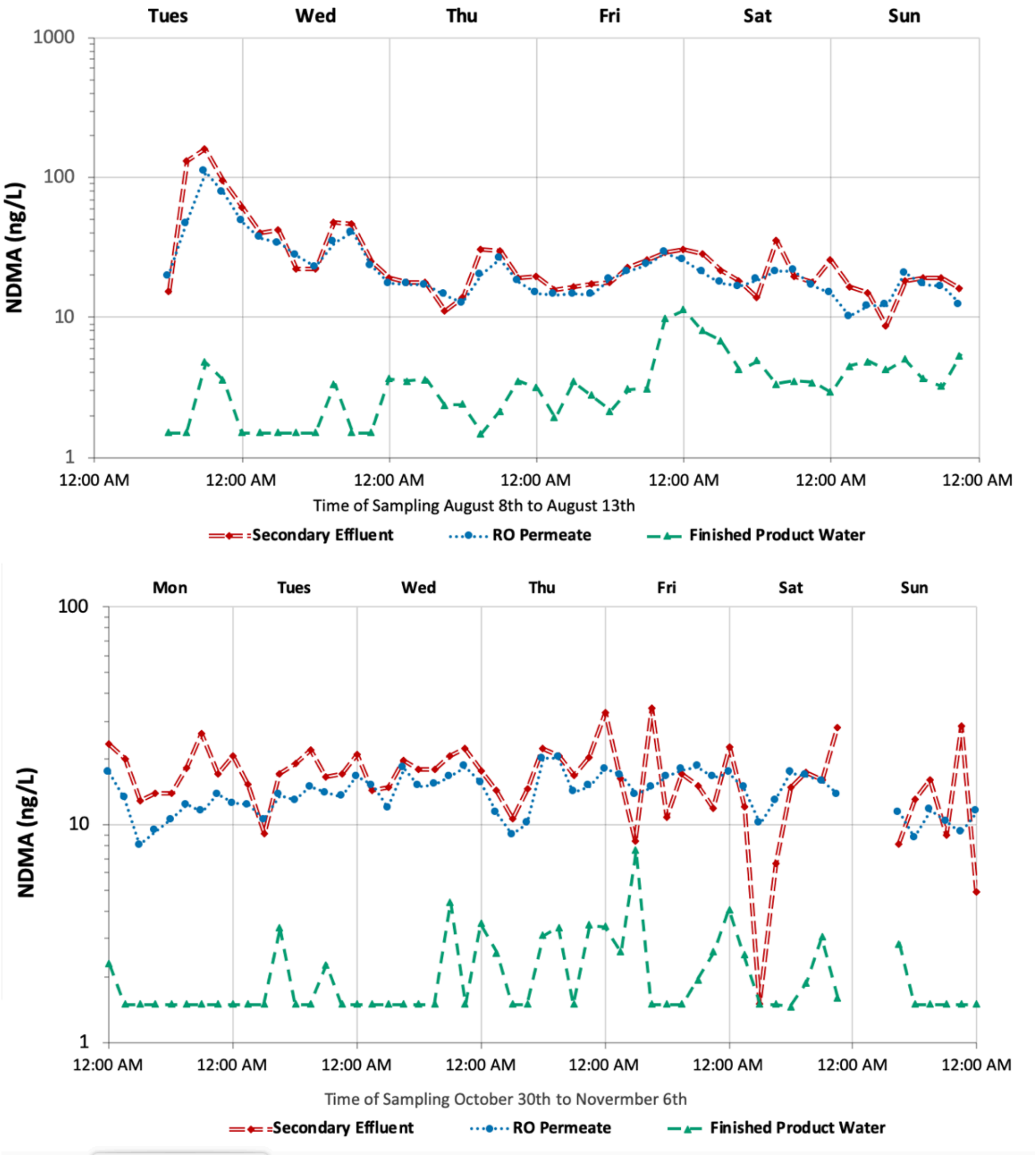


Figure 3. August (top) and November (bottom) 2017 NDMA concentration in the OCWD AWPF plant influent (secondary plant effluent), reverse osmosis (RO) permeate and finished product water over 5 or 7 consecutive days measured every 3 hours

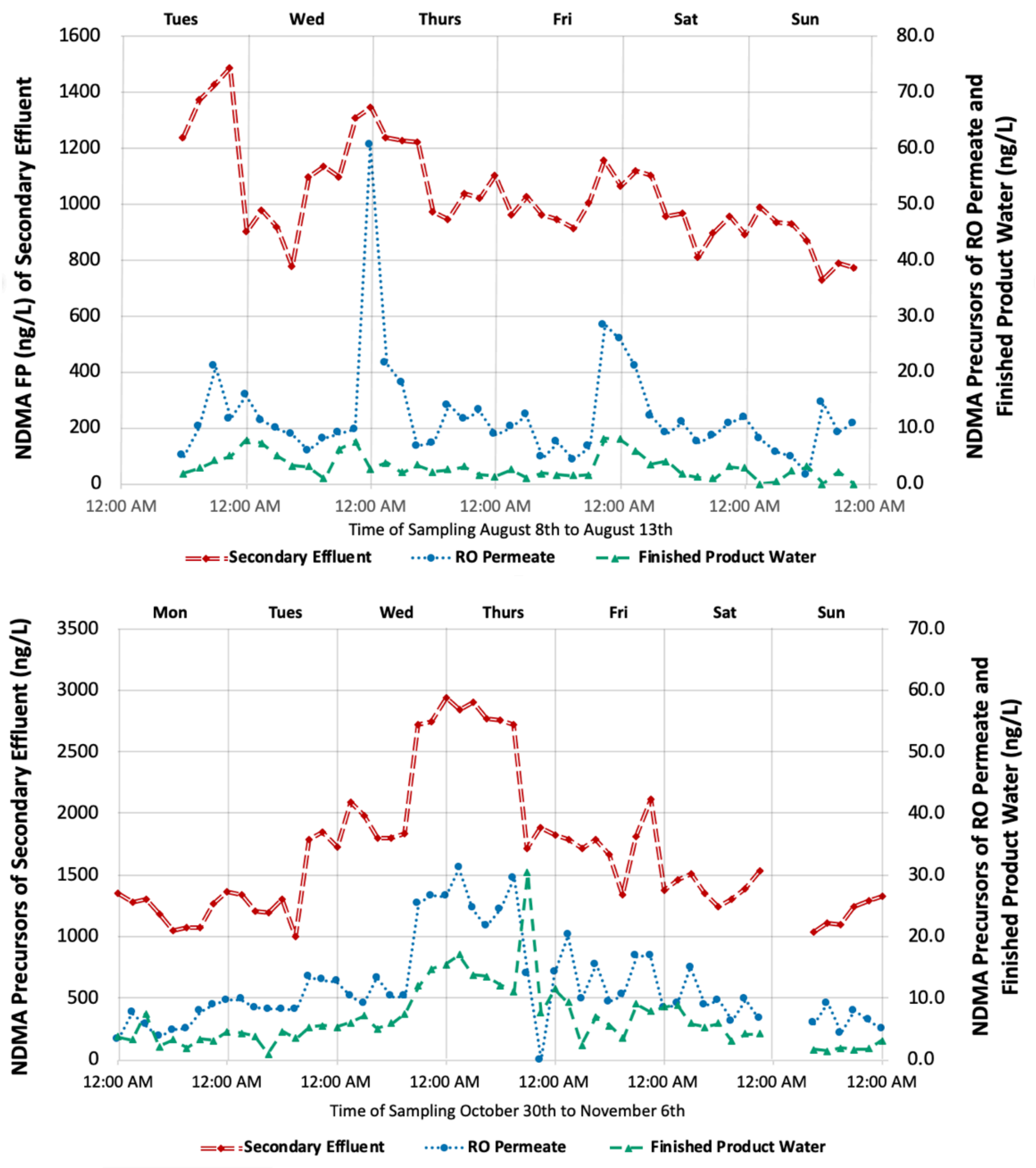


Figure 4. August (top) and November (bottom) 2017 NDMA precursors concentration (as formation potential, FP) in the OCWD AWPF plant influent (secondary plant effluent), reverse osmosis (RO) permeate and finished product water over 5 or 7 consecutive days measured every 3 hours

UV absorbance at 254 nm (a measure of aromatic organic matter) was also measured during both sampling events (Figure 5). As with NDMA and its precursors, UV_{254} concentration showed fluctuations throughout the sampling events in August and November – however, it did not mirror the NDMA or precursors, and the propagative trend through the different treatment processes was less evident, indicating that UV_{254} as a monitoring tool is not directly predictive of NDMA or NDMA precursor concentrations.

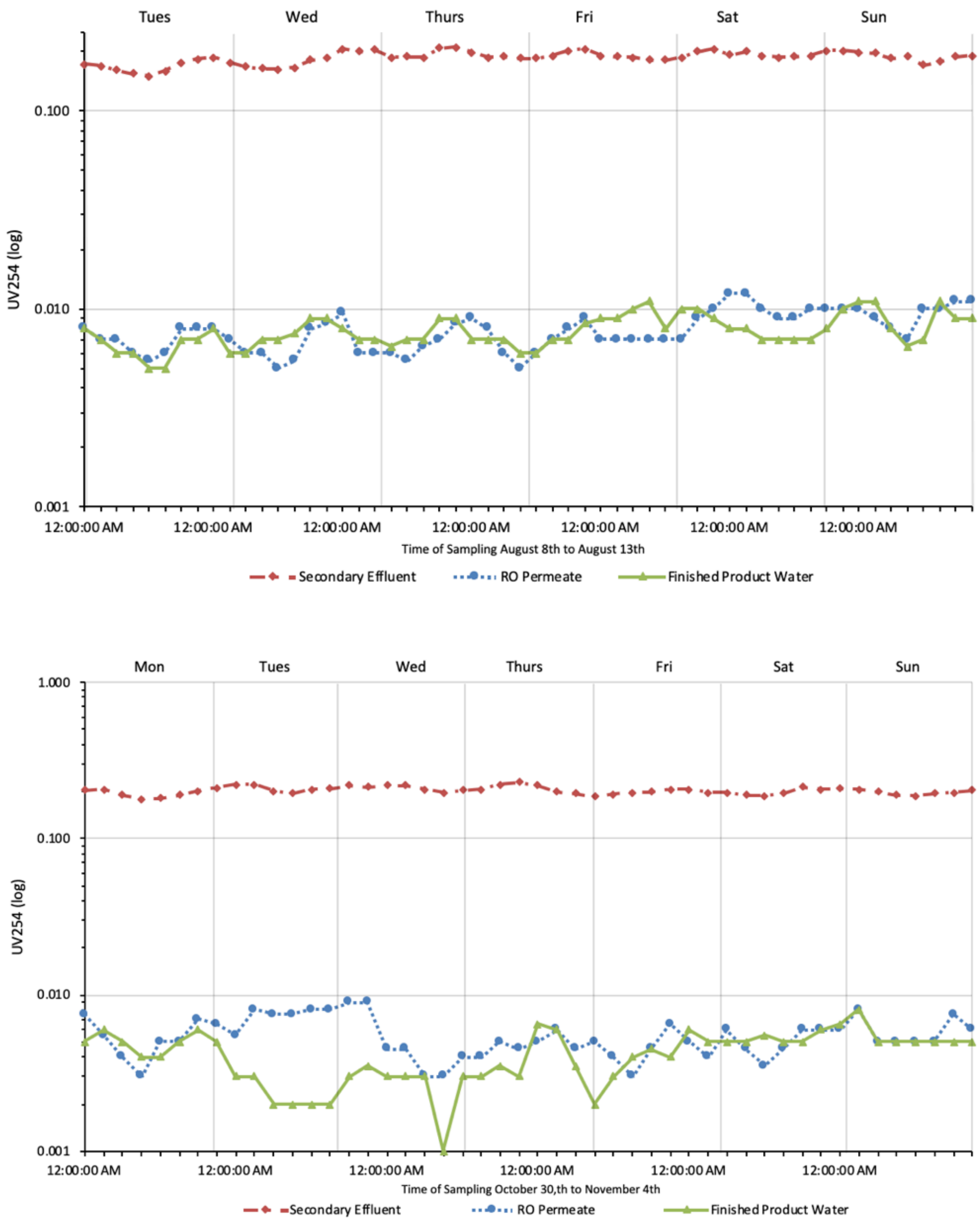


Figure 5. August (top) and November (bottom) 2017 UV_{254} concentration in the OCWD AWPF plant influent (secondary plant effluent), reverse osmosis (RO) permeate and finished product water over 5 or 7 consecutive days measured every 3 hours

The trends in NDMA and NDMA precursor concentration follow a similar pattern in the August event (i.e., NDMA peaks in the August event occur at similar times as the NDMA precursor peaks). However, there is a clear peak in NDMA precursor concentration near 12:00 a.m. on Thursday that is not accompanied by a peak in NDMA. This suggests that NDMA and NDMA precursor concentration may be linked in some cases but are not always linked. In the August event, NDMA and NDMA precursor concentrations are at their maximum on Tuesday (at the beginning of the week) and subsequently drop as the week progresses.

Contrasting the August 2017 event, the similarity between NDMA and NDMA precursor concentration variation is not apparent in the November 2017 event. NDMA concentration in the plant influent (secondary effluent) and RO permeate varies throughout the week but is not significantly higher at any point during the 7 day period. However, NDMA precursor concentrations clearly increase between Tuesday and Thursday, followed by a decline through the remainder of the week. Comparing sampling locations, the trend in NDMA precursor concentration propagates through the treatment train as seen for the August event.

As with the August 2017 sampling event, UV_{254} concentrations during the November 2017 sampling event do not appear to vary in concert with either NDMA or NDMA precursor concentrations.

Total chlorine concentrations (Figure 6 and Figure 7) were slightly higher in August than they were in November and the concentration variations were propagated from the RO permeate to the finished product water, dropping in intensity via the UV/AOP process. In August, NDMA concentration appeared to vary with total chlorine concentration; however, this trend was not apparent in November, suggesting that NDMA concentration in the RO permeate is not entirely dependent on chlorine concentration.

Electrical conductivity measurements (Figure 8) were similar in August and November, with a tendency to peak just before or just after 12:00 a.m. There were diurnal fluctuations; however, this variation was similar throughout the week.

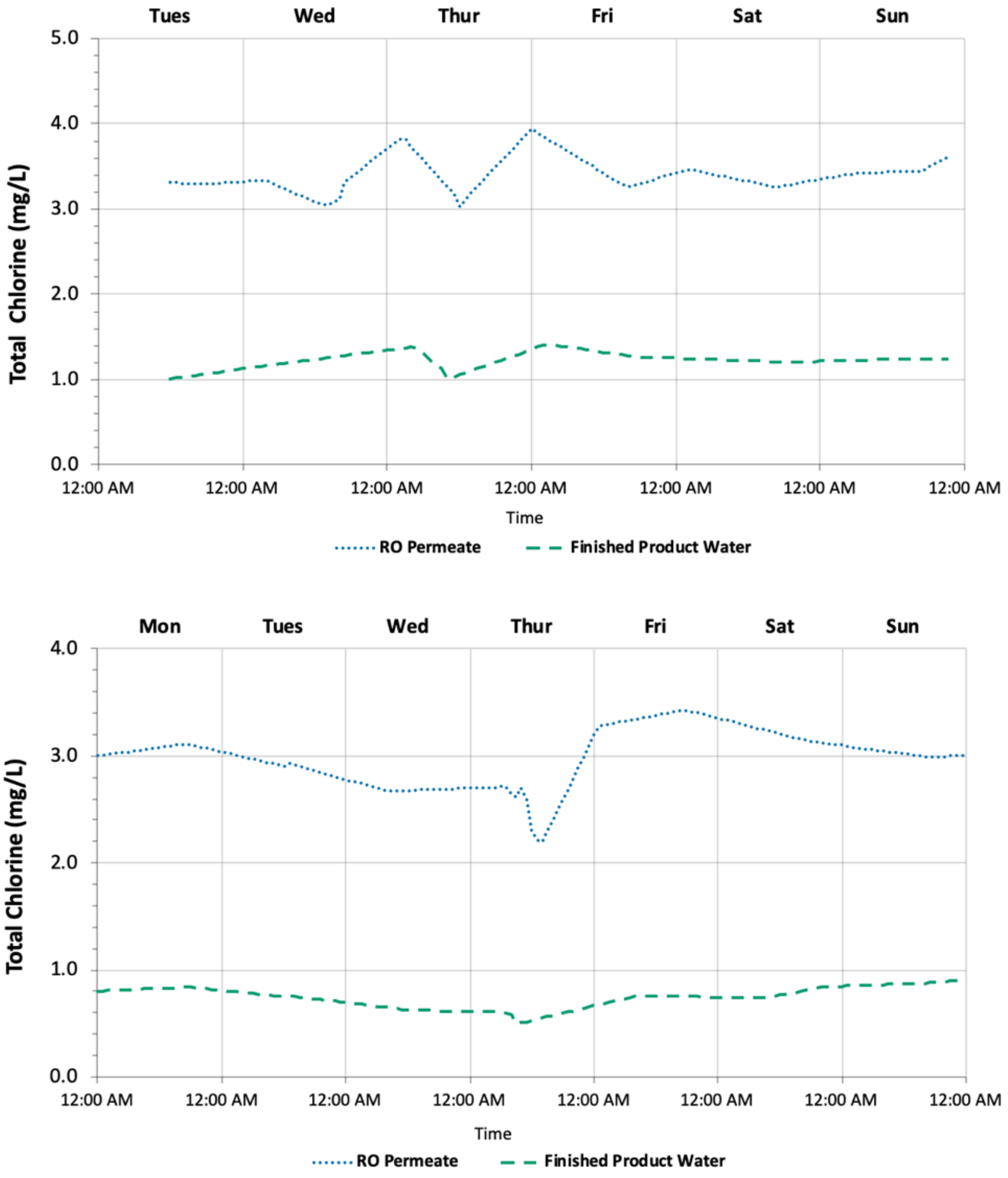


Figure 6. August (top) and November (bottom) 2017 total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate and finished product water over 5 or 7 consecutive days measured every 3 hours

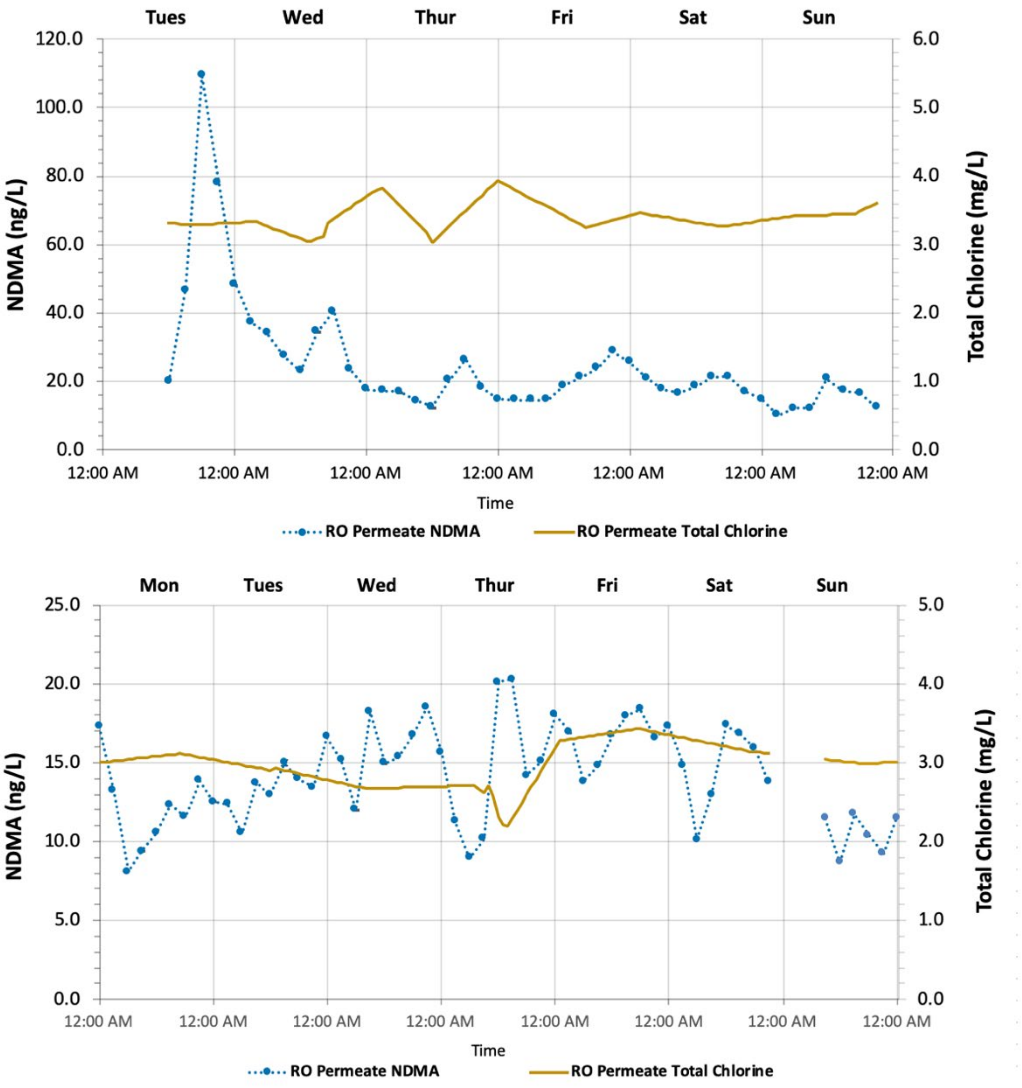
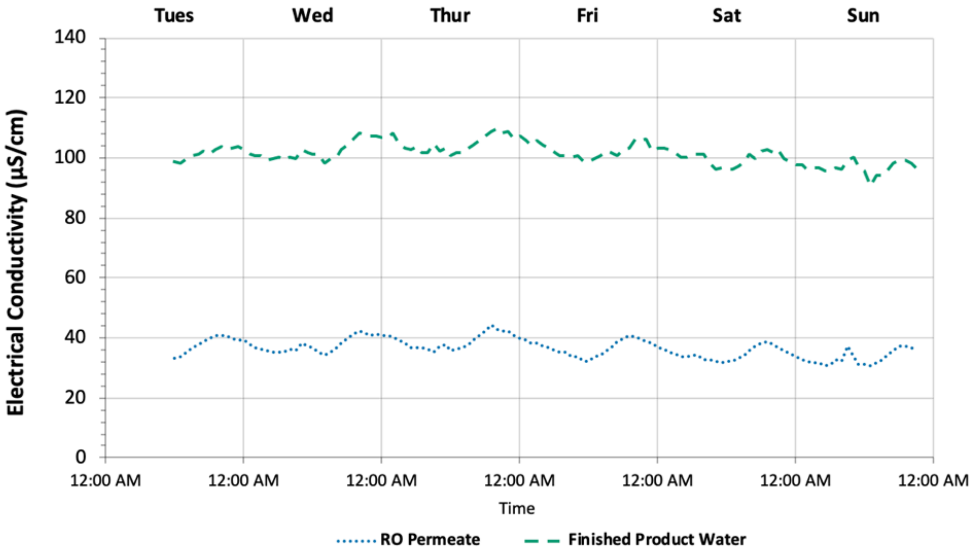


Figure 7. August (top) and November (bottom) 2017 total chlorine concentration and NDMA concentration in the OCWD AWPF reverse osmosis (RO) permeate over 5 or 7 consecutive days measured every 3 hours



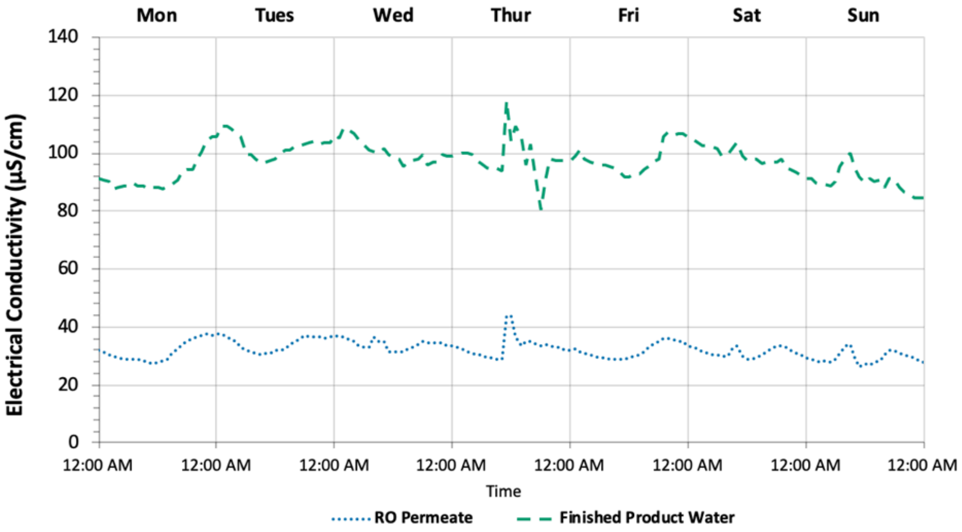


Figure 8. August (top) and November (bottom) 2017 electrical conductivity in the OCWD AWPF reverse osmosis (RO) permeate and finished product water over 5 or 7 consecutive days measured every 3 hours

3.1.2 NDMA Occurrence at OCWD AWPF (2019)

In 2019, samples were collected every 3 hours from the OCWD AWPF RO permeate, UV/H_2O_2 product water, and finished product water for 7 consecutive days on three separate occasions several weeks apart (September 2019, October 2019, and December 2019). At each site, concentrations of NDMA, total chlorine, and electrical conductivity were determined. Due to the large number of NDMA samples and to assess analytical error in this large data set, analytical duplicates were measured for a subset (20 percent) of samples. The detection limit for NDMA analysis was 1.2 ng/L. Values below the detection limit are plotted at 1.2 ng/L in the figures discussed below.

The primary objective was to assess diurnal variation of NDMA with respect to evaluation of the benefit of online monitoring for this compound. Other target constituents/parameters were also sampled for comparison purposes, though less frequently due to laboratory capacity limitations and cost. The additional sampled parameters involve halogenated DBPs, excitation emission matrix spectroscopy (EEMS), and CECs, with sampling and analysis procedures as follows:

- Halogenated DBPs were measured every 3 hours from each location over one 24-hour period during each of the three sampling events. Samples were collected and analyzed in triplicate.
- In each event, EEMS were generated for a subset of samples. On two of the seven days, RO permeate and finished product water samples were evaluated every three or six hours.

Two additional sample events were completed. One event was completed in May 2018 which evaluated concentrations of halogenated DBPs every 3 hours over one 24-hour period. Another event was completed at a second advanced water treatment plant (PDMWD's Advanced Water Purification Demonstration Facility) to assess potential differences between treatment facilities. Samples were collected every 3 hours during a 10-hour day for 3 days and analyzed for NDMA concentration.

3.1.2.1 Event 1 (May 2018: Halogenated DBPs Only)

Samples were collected every 3 hours over a 24-hour period from the plant influent/secondary wastewater treatment plant effluent (Q1), RO feed, RO permeate, UV product water, and finished product water and analyzed for additional disinfection byproducts. Four trihalomethanes (THMs) [bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM), and trichloromethane (TCM)] and three haloacetic acids (HAAs) [bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA)] were measured (Figure 9 and Figure 10). Concentrations of all THMs and two of the three HAAs were near the detection limit (DL) in the plant influent (prior to chlorine addition). The relevant DLs were as follows: TCM at 0.3 ppb, BDCM at 0.02 ppb, DBCM at 0.02 ppb, TBM at 0.02 ppb, BCAA at 0.2 ppb, DCAA at 0.6 ppb, and TCAA at 0.2 ppb. These all increased in RO feed water (after chlorine addition) and then decreased again to at or below the detection limit after RO (RO permeate). The exception was TCAA, which was present in the plant influent. However, TCAA increased in concentration after chlorine addition as well. BDCM, DBCM, and TCM all increased in concentration in the RO feed between 3:00 a.m. and 9:00 a.m. and decreased between 9:00 a.m. and 6:00 p.m. TBM had an opposite trend, decreasing between 12:00 a.m. and 12:00 p.m. and increasing after 12:00 p.m. The HAAs DCAA and TCAA followed a similar pattern of fluctuation in the RO feed throughout the 24-hour period, generally decreasing between 6:00 a.m. and 9:00 a.m. and increasing between 9:00 a.m. and 9:00 p.m. BCAA was at or below the detection limit at all time points except 6:00 a.m., when there was a slight increase in the RO feed.

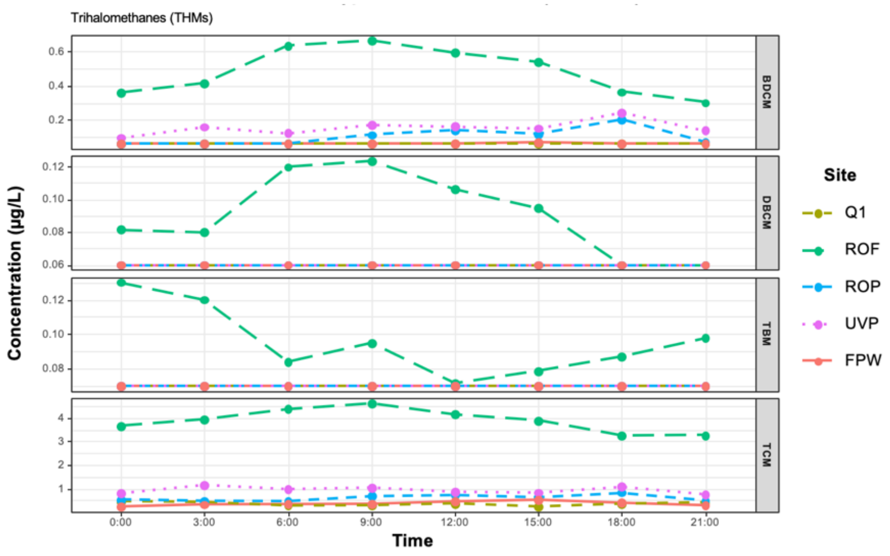


Figure 9. Trihalomethane concentration [bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM), and trichloromethane (TCM)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

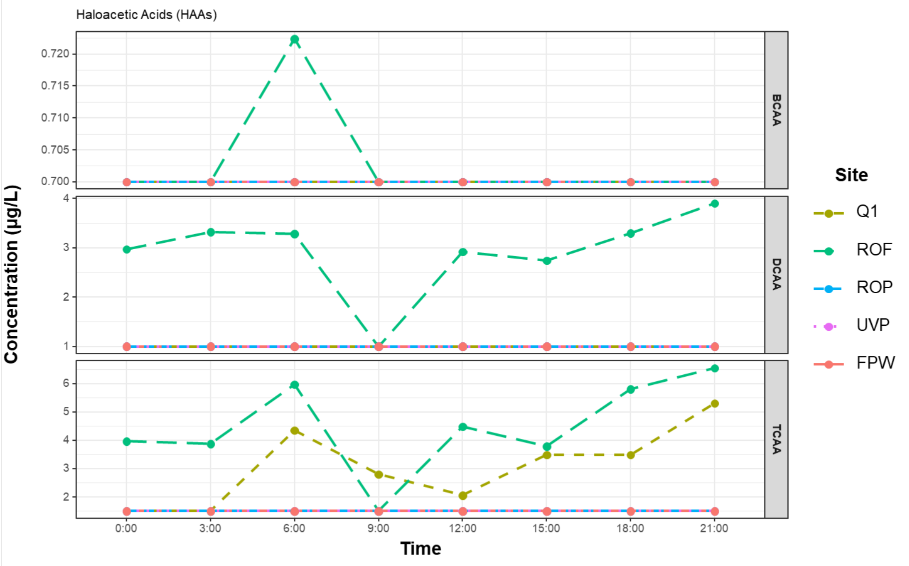


Figure 10. Haloacetic acid concentration [bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

3.1.2.2 Event 2 (September 2019: NDMA, Halogenated DBPs, EEMs, Electrical Conductivity, and Total Chlorine)

In the September 2019 event, NDMA concentration appeared to propagate through the OCWD AWPF treatment train (see Appendix A, Figure i). NDMA concentration appeared to peak each day around 9:00 p.m. and then declined after midnight. This trend was similar for the August

2017 and November 2017 sampling events, with NDMA peaks for the day tending to occur in the evenings.

Interestingly, an NDMA peak occurring on Wednesday appeared to be completely eliminated after UV-AOP treatment; however, a similar peak was observed in the finished product water. This suggests that although UV-AOP is effective at removing NDMA, NDMA concentration can increase in the finished product water if the precursors that created the spike in NDMA concentration are not removed by UV-AOP. At this facility, finished product water refers to the UV-AOP product water after lime addition and partial decarbonation performed to achieve an elevated pH (pH approximately 8.5) for corrosion control. This practice is utilized to increase the pH of the water prior to its entrance into cement-mortar-lined pipelines which may degrade over time if exposed to low alkalinity water having low pH. However, NDMA formation is pH dependent with pH above approximately 8.0 producing NDMA much more efficiently (Leavey-Roback et al. 2016a; Schreiber and Mitch 2005). Thus, increasing the pH after UV-AOP has the potential to allow for the formation of NDMA assuming all or most of the precursors have not been removed, as noted in prior studies.

A second peak in NDMA concentration was observed on Sunday, although there was no discernable trend in NDMA concentration throughout the week (it did not steadily rise, fall, or peak throughout the week). However, the peak on Sunday was not removed in the UV product water and it then decreased in the finished product water. This is likely a sampling error (e.g., UV-AOP feed water collected on this day instead of UV-AOP product water), since a reduction in NDMA between UV product water and finished product water is not expected, and otherwise UV-AOP consistently generates near non-detect or non-detect levels of NDMA. Nevertheless, the observations reveal that when a higher-than-normal peak in NDMA occurred in the RO permeate (Sunday), it corresponded to a peak in the finished product water that exceeded water quality objectives (10 ng/L NDMA), while an earlier peak in NDMA (Wednesday) did not lead to a finished water exceedance (finished water peak was discernable but below 10 ng/L). Since plant operation is typically very consistent, the variability in peak propagation to the finished water is likely due to a changing background water quality (e.g. NDMA precursor concentration, which is known to vary dramatically per 2017 data in Figure 4).

Total chlorine in the RO permeate varied over the course of the week. The OCWD online plant analyzer measures total chlorine which can be assumed to be in the form of chloramines (i.e., no or insignificant free chlorine concentration). Total chlorine tended to be at its lowest concentration in the morning. The total chlorine trend tended to not propagate through treatment, likely due to the destruction of chlorine during the UV-AOP process. Of note is the correlation between NDMA and total chlorine (see Appendix A, Figure iii), in which NDMA concentration in the RO permeate varied according to total chlorine concentration. This suggests that as chlorine concentration increases at AWPF, NDMA formation will increase correspondingly; this is not surprising given that NDMA formation occurs as a result of reaction between chloramine and NDMA precursors. Increased chlorine dosing may also be utilized when water quality declines and, thus, chlorine demand increases. In this case, the lower water quality could also indicate a greater load of precursors, although this is not necessarily the case.

Electrical conductivity (EC) also varied throughout each day. The trend in EC concentration appeared to propagate from RO permeate through the finished product water. However, EC concentration was reduced between these two sample points.

Other DBPs were measured in the RO permeate UV product water and finished product water over one 24-hour period every 3 hours during this sampling week. The concentrations of the THMs varied throughout the period with concentrations of ND to approximately 0.75 ppb for BDCM, approximately 0.15 ppb for DBCM, and 2.0 ppb for TCM (see Appendix A, Figure v). These concentrations are far below the 80 ppb EPA Maximum Contaminant Level (MCL) for total trihalomethanes. Similarly, HAAs varied slightly throughout the week. However, the only HAA with a measurable concentration in the finished product water was MBAA with a maximum concentration of approximately 1.1 ppb. The MCL for five HAAs (HAA5) is 60 ppb. Thus, despite fluctuation of these other DBPs, concentrations remained well below MCLs.

3.1.2.3 Event 3 (October 2019: NDMA, Halogenated DBPs, EEMs, Electrical Conductivity, and Total Chlorine)

In the October 2019 sampling event, NDMA concentration varied throughout the week, peaking late Friday evening. NDMA concentration tended to be at its highest level between 6:00 p.m. and 12:00 a.m. each day. As was seen for the other sampling events, NDMA concentration was reduced to below or near the detection limit by UV-AOP but then increased in the finished product water (after pH adjustment) due to NDMA rebound. The trend in NDMA concentration in finished product water was somewhat similar to the trend in the RO permeate (i.e., propagation of peaks), suggesting that some of the NDMA precursors present in the RO permeate are not removed by UV-AOP. Prior studies have shown that UV-AOP only partially reduces the concentration of NDMA precursors (Roback et al. 2019).

Total chlorine concentration was highly variable in the RO permeate during this event, with less variation in the UV product and finished product water. NDMA concentration varied with total chlorine concentration during certain days of the week; however, this trend was not consistent, again underscoring the idea that NDMA may be influenced by total chlorine concentration while not being entirely dependent on this factor.

Similar to previous events, electrical conductivity varied from day to day while remaining within a similar range throughout the week.

DBP concentrations ranged from ND to approximately 1.1 ppb for the THMs and ND to 8 ppb for the HAAs in the finished product water. Concentrations fluctuated throughout the week and the UV-AOP process did not appear to be highly effective in removing the majority of the DBPs.

3.1.2.4 Event 4 (December 2019: NDMA, Halogenated DBPs, EEMs, Electrical Conductivity, and Total Chlorine)

For Event 4, NDMA concentration peaked on Thursday and was at its lowest concentration between Sunday and Monday, similar to Event 3 and the August 2017 sampling event. Event 2 had a similar decline in concentration over Saturday and Sunday; however, there was an increase late Sunday. The November 2017 event is the only event that did not show a general decline in NDMA concentration during Saturday and Sunday, suggesting that this trend is likely significant and occurring on an at-least semi-regular basis. The reason for the decrease in NDMA concentration during the weekend may be linked to a decline in the input of NDMA precursors during these days. This suggests that processes or business practices that are specific to weekdays may be sources of NDMA precursors.

Total chlorine concentration was variable throughout the week and propagated from the RO permeate to the UV product water and finished product water. Similar to the August 2017 sampling event and the October 2019 event, NDMA concentration appeared to vary with total chlorine concentration, suggesting the trend occurs frequently.

EC also varied from day to day, but the variation remained stable throughout the week.

DBP concentrations varied throughout the 24-hour period and ranged from ND to approximately 2 ppb for the THMs and from ND to approximately 1.3 ppb for the HAAs. A more limited panel of three THMs and two HAAs were analyzed in this sample event to reduce the analytical sample load as previous sample events showed the same trends.

3.1.2.5 Padre Dam Municipal Water District (March 2018: NDMA)

Sampling of an additional advanced treatment facility was completed for comparison. PDWMD operates an Advanced Water Purification Demonstration Facility in San Diego County, California. The 100,000 gallon per day plant utilizes MF, followed by RO and UV-AOP using free chlorine (Figure 2). Samples were collected and analyzed for NDMA on three consecutive days (Monday, Tuesday, and Wednesday, March 12 through March 14, 2019) every 3 hours during a 10-hour period from 6:00 a.m. to 4:00 p.m. Plant influent (treated wastewater effluent), RO feed, and RO permeate water were collected.

The results for all dates and sites are shown in Figure 11. NDMA concentration in the plant influent was the highest on Monday and increased from 6:00 a.m. to 4:00 p.m. This increase propagated from the plant influent through the RO permeate. On the other two days, plant influent NDMA concentration slightly declined throughout the day. The trends tended to propagate through the treatment train except for one peak in the NDMA concentration in the RO permeate on Tuesday. It is likely that the lack of diurnality (peaks) in the NDMA concentration compared to the OCWD sampling results (e.g., Figure 3) is due to the shorter sampling periods, since at OCWD the rise in NDMA concentration lasted nearly a half day before the "peak" began to fall, falling for hours before rising again.

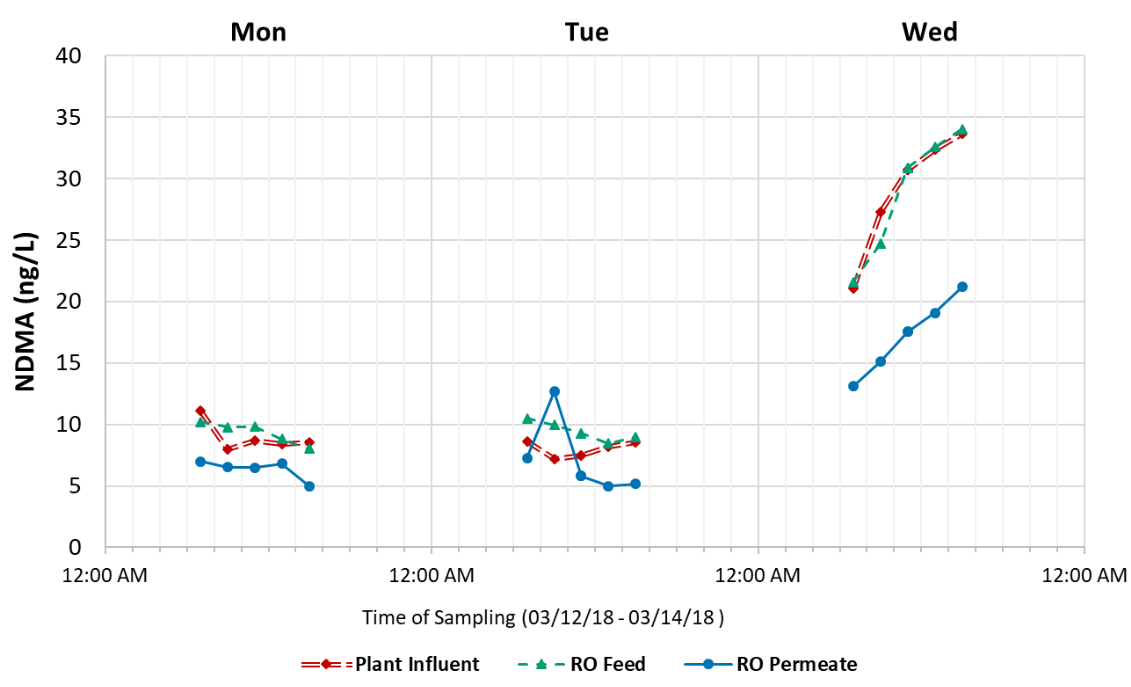


Figure 11. NDMA concentration in the PDMWD plant influent (wastewater treatment plant effluent), reverse osmosis (RO) feed, and RO permeate over 3 consecutive days (measured every 3 hours during a 10-hour period)

3.1.3 Correlations with Potential Surrogates

UV_{254} is commonly used as a surrogate for the presence of bulk aromatic organic material that occurs as a mixture of many individual organic compounds. It has been used frequently to assess the nature of natural organic matter in drinking and wastewater treatment plants (Ulliman et al. 2020). Similarly, TOC is a commonly used surrogate for the presence of organic compounds and indicates the total concentration of organics.

For this study, UV_{254} absorbance values were determined at each sampling point during the two 2017 sampling events (not the 2019 sampling events). TOC measurements were also collected via online monitors at certain sampling locations. UV_{254} and TOC concentrations were compared to NDMA and NDMA precursor concentrations at the matched sample points to determine whether either of the two constituents could be useful as a surrogate for NDMA or NDMA precursors. Pearson correlation coefficients were calculated to assess the relationships among these various parameters. No correlations greater than 0.5 were found in the comparisons of the constituents listed in Table 1 and Table 2. This indicates that these parameters, while useful for general organic character and concentration monitoring at potable water treatment plants, are not useful indicators (predictors) of the presence of either NDMA or NDMA precursors.

Table 1. Pearson correlation coefficient values for given variables (August 2017 sampling event)

Site	NDMA v. NDMA FP	NDMA v. UV 254	NDMA v. TOC	NDMA FP v. UV 254	NDMA FP v. TOC
Plant Influent	0.5	-0.2	0.5	-0.3	-0.1
RO Permeate	0.1	0.2	0.2	0.5	0.0
Finished Product Water	0.1	0.3	-0.1	0.0	-0.9

Table 2. Pearson correlation coefficient values for given variables (November 2017 sampling event)

Site	NDMA v. NDMA FP	NDMA v. UV 254	NDMA v. TOC	NDMA FP v. UV 254	NDMA FP v. TOC
Plant Influent	0.1	0.3	NM	0.3	NM
RO Permeate	0.4	-0.1	0.3	-0.2	0.3
Finished Product Water	0.1	0.2	NM	0.0	NM

NM = not measured

3.1.4 Excitation Emission Matrix Spectroscopy

Excitation emission matrix (EEM) spectroscopy was measured using a Horiba Aqualog and analyzed with the Solo software package from Eigenvector Inc. Results were preprocessed by normalizing values using a DI water blank and applying inner filter effect as well as first and second order Rayleigh masking. The data were then deconstructed using parallel-factor analysis which was able to identify four major components. The four components were individually identified using reference spectra from Chen et al. (2003).

As shown in Figure 12 and Figure 13, aromatic protein, fulvic-like, humic-like, and tryptophan-like components were measured over 2 days in the RO permeate and finished product water during Event 3 and Event 4. All components were typically at higher concentration in the RO permeate than in the finished product water, showing removal during UV-AOP.

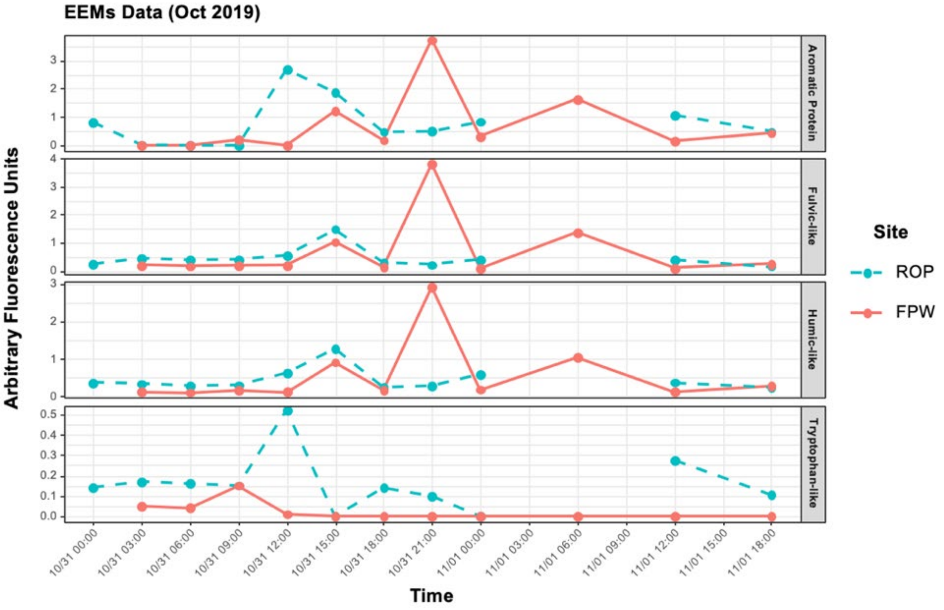


Figure 12. Aromatic protein, fulvic-like, humic-like, and tryptophan-like organic matter (EEM spectroscopy) in RO permeate (ROP) and finished product water (FPW) measured over 2 days every 3 hours

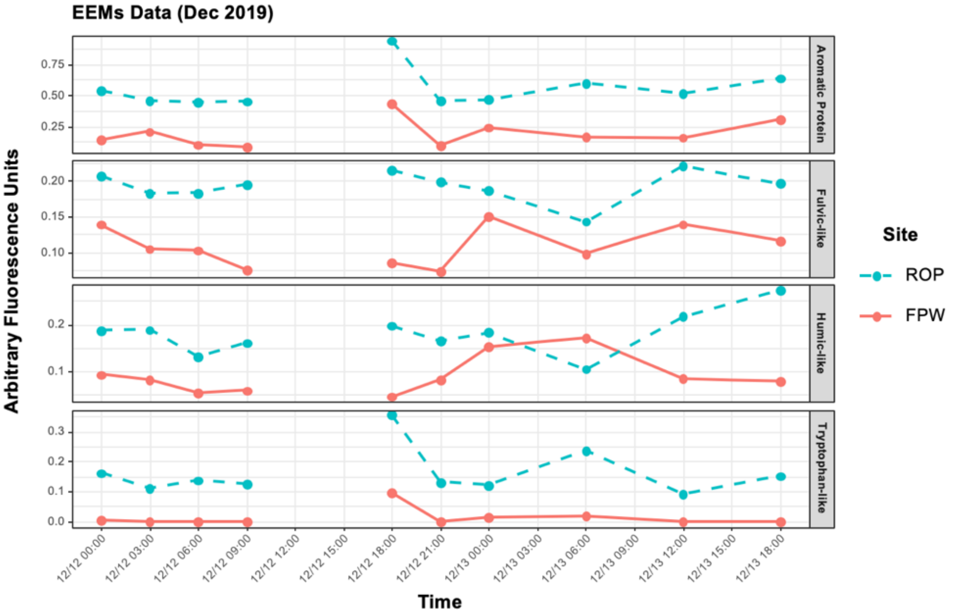


Figure 13. Aromatic protein, fulvic-like, humic-like, and tryptophan-like organic matter (EEM spectroscopy) in the RO permeate (ROP) and finished product water (FPW) measured over 2 days every 3 hours

The components showed diurnal variability similar to other water quality components. In Event 3 (October 2019), there was a peak in the finished product water at 9:00 p.m. for all components, except tryptophan-like, that exceeded the concentration in the RO permeate. This is unexpected, since UV-AOP (located after RO and before the FPW sampling site) improves water quality; this could suggest some introduction of organics into the water after RO or a shift in organic character related to UV-AOP treatment.

3.2 NDMA Precursor Occurrence and Fate in Advanced Treatment Facilities

To better understand the loading and removal of NDMA precursors at advanced water treatment facilities, samples were collected on five occasions from two advanced water treatment plants, OCWD GWRS AWPF (Figure 1) and PDMWD Advanced Water Purification Demonstration Facility (Figure 2). Samples were analyzed for NDMA and NDMA precursors after each stage of treatment. Grab samples were collected in duplicate and standard deviations are indicated in the figures referenced below.

3.2.1 OCWD Events 1 and 2 (August and November 2017)

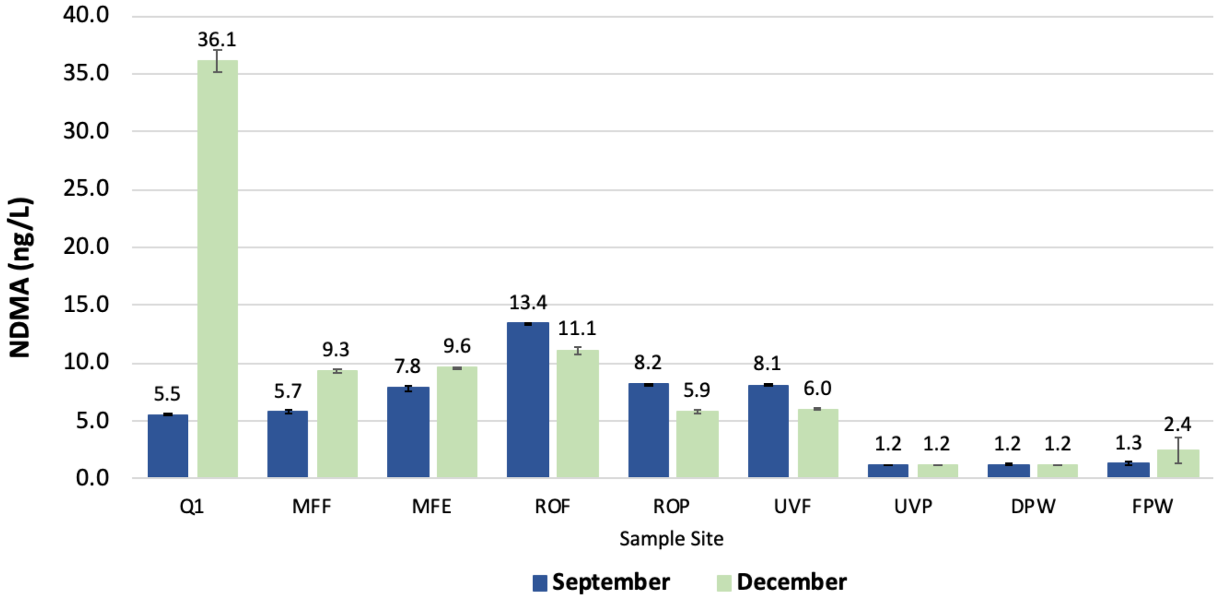
NDMA formation potential tests to determine NDMA precursor occurrence were completed in August and November of 2017. The results are reported in Section 3.1.1. Additional sampling for NDMA precursors was completed in 2019 as described in the next section.

3.2.2 OCWD Event 3 (September 2019)

The occurrence of NDMA at the OCWD GWRS AWPF is shown in Figure 14 for the September 2019 sampling event (Event 3). Chlorine (to form chloramines) is dosed to after the plant influent (Q1) sampling site to the microfiltration feed water (MFF) for biofouling control during MF and RO. NDMA was found in a relatively low concentration in the plant influent (Q1) and the concentration increased after the addition of chlorine (MFF sample); the concentration further increased in the RO feed sample, which is located approximately 8 minutes of travel time (under normal operating conditions) after the microfiltration effluent (MFE) location. NDMA in Q1 typically ranges from approximately 10 ng/L to as high as approximately 150 ng/L, with an average of approximately 25 ng/L. This allows time for the NDMA formation reaction (in which chloramine and NDMA precursors react to form NDMA), resulting in an increased concentration of NDMA in the RO feed sample.

Comparing RO feed and permeate concentrations in this event, RO removed approximately 39 percent of the NDMA. Previous data from this AWPF indicate that typical RO removal of NDMA ranges from approximately 20 to 65 percent (Roback et al. 2018a). Comparing UV-AOP feed and product water, the UV-AOP process removed NDMA to below the 1.2 ng/L detection limit, as expected. A major driver for the inclusion of UV treatment in advanced purification facilities is removal of NDMA. The NDMA concentration in UV-AOP product water remained non-detect after decarbonation. Along with partial decarbonation, lime is added to the water as a final step in the treatment process in order to increase the pH for corrosion control. This pH increase resulted in an increase in NDMA concentration, although the increase was small

(NDMA rebound). Prior studies at this facility had confirmed that the lime itself does not add NDMA (i.e., via impurities).



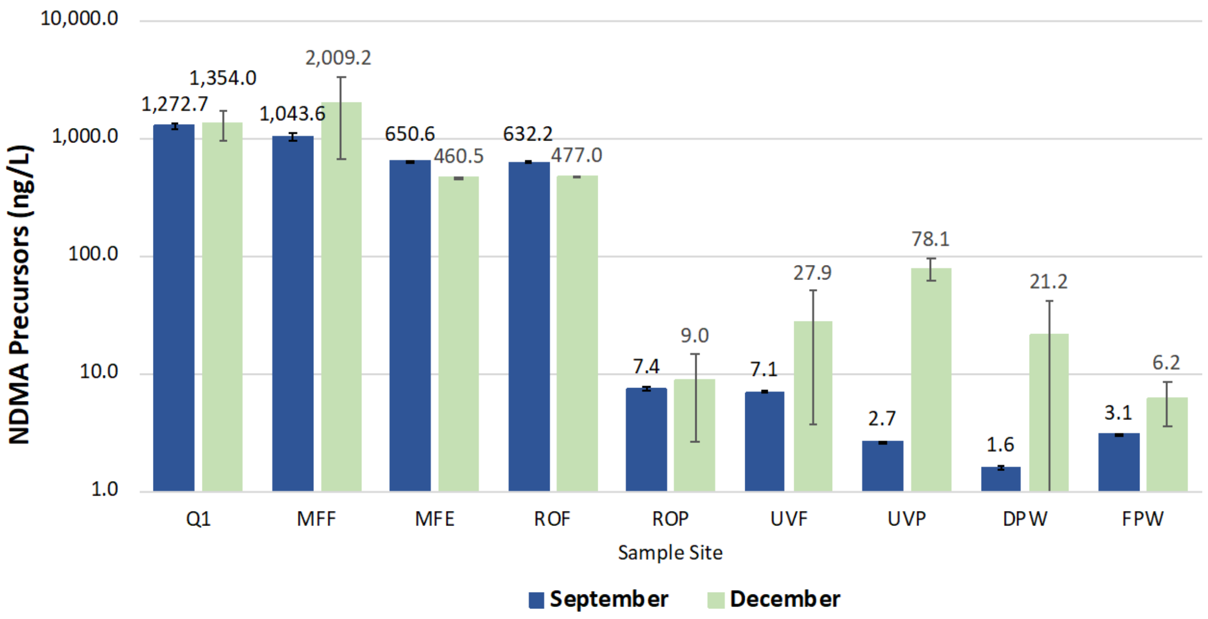
Sampling site nomenclature: Q1 = influent to the advanced treatment facility, which is OCSD secondary treated wastewater effluent prior to chlorination; MFF = microfiltration feed, which is Q1/influent after chlorine addition to form chloramines; MFE = microfiltration effluent; ROF = reverse osmosis feed, which is MFE after sulfuric acid and antiscalant addition, both to reduce scaling; ROP = RO permeate; UVF = UV/H_2O_2 system feed water, which is ROP after H_2O_2 addition; UVP = UV/H_2O_2 system product water; DPW = decarbonated product water, which is UVP that has been decarbonated to increase pH for corrosion control; FPW = finished product water, which is a blend of UVP (DPW bypass) and DPW, then lime addition to the blend for corrosion control.

Figure 14. NDMA concentration in OCWD GWRS AWPF at each stage of treatment (September 30 and December 10, 2019)

The occurrence of NDMA precursors at the OCWD GWRS AWPF is shown in Figure 15 for the same September 2019 sampling event in which NDMA was measured. NDMA precursor concentration was high in the plant influent (Q1) through to the RO feed. RO significantly eliminated NDMA precursors. NDMA precursor concentration was reduced from 632 to 7.4 ng/L, or by 98.8 percent. Prior to RO, NDMA precursor concentration was also reduced by microfiltration (comparing MFF and MFE sample), which corresponded to an increase in NDMA concentration in MFE (Figure 14). This is a result of NDMA precursors being converted to NDMA after the chlorine addition to the MF feed water. NDMA precursor concentration was reduced by approximately 400 ng/L between MFF and ROF, but NDMA concentration is increased by only 7.7 ng/L. This indicates that the reduction of NDMA precursors across MF is not attributable to NDMA formation. The reduction could be due to complete oxidation of NDMA precursors by the high dose (approximately 10 mg/L) of chlorine. This is because many NDMA precursors are oxidized by free chlorine to transformation products that do not form NDMA (Shah et al. 2012; Leavey-Roback et al. 2016b). Due to the high dosing of chlorine at this location, a portion of the chlorine/chloramine mixture present is temporarily in the form of free chlorine which facilitates this reaction. Additionally, the removal of NDMA precursors across MF could be attributed to sorption of these organic compounds to the membrane cake layer (accumulated foulant) on the membrane feed side during filtration and/or sorption to the particles filtered out by MF that exceed the 0.2 um pore size (as evidenced by significant turbidity and total suspended solids reduction by MF, which is pretreatment to RO).

UV-AOP removed some NDMA precursors, approximately 4 ng/L or 62 percent. This indicates that UV-AOP may be effective at removing some NDMA precursors. However, not all NDMA precursors are susceptible to ultraviolet light or advanced oxidation by hydroxyl radicals.

Interestingly, there was a 41 percent reduction of NDMA precursors by decarbonation (DPW sample), though this is only 1.1 ng/L due to the very low levels by the end of the purification process. This suggests that air stripping is potentially effective to remove a significant portion of NDMA precursors (presumably, those that are volatile) and warrants further study to confirm these findings. Decarbonation is not intentionally utilized for purification at this facility, but rather for corrosion control to increase pH. However, air stripping of finished water has been suggested for consideration for direct potable reuse facilities as a further barrier to unknown organics or for aberrant TOC peaks from illegal/unintentional sewershed discharges, especially if decarbonation is required for corrosion control in any case. This is because direct reuse would omit the environmental buffer (groundwater aquifer) such as utilized for the OCWD indirect reuse facility. In the OCWD AWPF, decarbonation only occurs for approximately 20 percent of the finished water flow (as a function of balancing pH and lime-related alkalinity to meet specific corrosion index targets), and thus the precursor control benefit is not fully realized. For this reason, the finished water concentration of precursors was slightly higher than DPW (Figure 15) and more similar to UV-AOP product water, since the finished water is an approximate 80/20 UVP/DPW blend with subsequent lime addition.



Sampling site nomenclature: Q1 = influent to the advanced treatment facility, which is secondary treated wastewater effluent prior to chlorination; MFF = microfiltration feed, which is Q1/influent after chlorine addition to form chloramines; MFE = microfiltration effluent; ROF = reverse osmosis feed, which is MFE after sulfuric acid and antiscalant addition, both to reduce scaling; ROP = RO permeate; UVF = UV/H_2O_2 system feed water, which is ROP after H_2O_2 addition; UVP = UV/H_2O_2 system product water; DPW = decarbonated product water, which is UVP that has been decarbonated to increase pH for corrosion control; FPW = finished product water, which is a blend of UVP (DPW bypass) and DPW, then lime addition to the blend for corrosion control.

Figure 15. NDMA precursor concentration in OCWD GWRS AWPF at each stage of treatment (September 30 and December 10, 2019)

3.2.3 OCWD Event 4 (December 2019)

For OCWD Event 4, NDMA was removed to below the detection limit by the UV/AOP process and increased after pH adjustment in the finished product water, similar to OCWD Event 3. However, the amount and trends of NDMA precursors in Event 4 differ significantly from previous events. While NDMA precursors were removed significantly by RO, after the addition of hydrogen peroxide (UVF) and again after the UV/AOP process (UVP), there was a significant increase in NDMA precursors. No work has shown that hydrogen peroxide can form NDMA precursors; however, as an oxidant, this is a possibility. Another possibility is that precursors are not created by the hydrogen peroxide addition but are added to the water as a contaminant in the hydrogen peroxide solution. Additionally, previous studies have shown that the UV photolysis process can create new NDMA precursors (Radienovic et al. 2012), so the increase seen here may be attributed to that factor. However, past work at pilot-scale by the research team has shown that NDMA precursors are consistently reduced in concentration by UV-AOP, not increased/formed, although the degree of removal is highly variable, ranging from less than 10 percent removal to complete removal (Hokanson et al. 2019). Thus, the increase shown in December 2019 for the AWPF sampling is unexpected. Although samples were collected using

LaGrangian sampling to follow a plug of water, it is possible that there was a fluctuation in the flow rate of water through the plant resulting in a plug of water with a higher concentration of NDMA precursors being collected in the UV feed sample; however, this seems unlikely.

After UV-AOP, the concentration of precursors is reduced in the decarbonated and finished product water. One reason for this could be the transformation of those precursors into NDMA. Not all of the NDMA produced in a formation potential test will be converted into NDMA in a real-world scenario (AWPF). The high molar conversion of the precursors in a formation potential test with 18 mg/L of monochloramine may be higher than what is seen at AWPF when the monochloramine concentration is less than 5 mg/L, and thus it is understandable that the total load of precursors seen in the UV product water will not be directly proportional to the concentration of NDMA in the finished product water. It may be the case that the concentration of precursors in the finished product water is reduced as certain precursors are converted to NDMA.

3.2.4 PDMWD Event 1 (October 2019)

The occurrence of NDMA at the PDMWD Advanced Water Purification Demonstration Facility is shown in Figure 16. NDMA concentrations did not vary as significantly at PDMWD compared to OCWD. NDMA concentration increased only slightly after chlorine addition. RO removed approximately 2 ng/L of NDMA (37 percent) and UV-AOP (UV/HOCl) removed no NDMA. This is surprising, as UV-AOP is the primary removal mechanism for NDMA at advanced water treatment facilities. Of importance, PDMWD utilizes sodium hypochlorite (NaOCl) as the oxidant in the UV-AOP system instead of hydrogen peroxide, which is used at OCWD. The NaOCl imparts free chlorine, monochloramine, and dichloramine species in the UV feed water. Mono- and dichloramine react with any remaining NDMA precursors present in the water to create NDMA. Thus, adding the NaOCl at this treatment step increases the opportunity for NDMA to form both before and immediately after the UV-AOP process; it is likely that the NDMA present in the UV product water is the result of the free chlorine dosing. A similar phenomenon was observed at OCWD in pilot testing with NaOCl (Hokanson et al. 2019; Roback et al. 2019). This is concerning because a number of potable reuse plants currently in development are considering UV/HOCl systems.

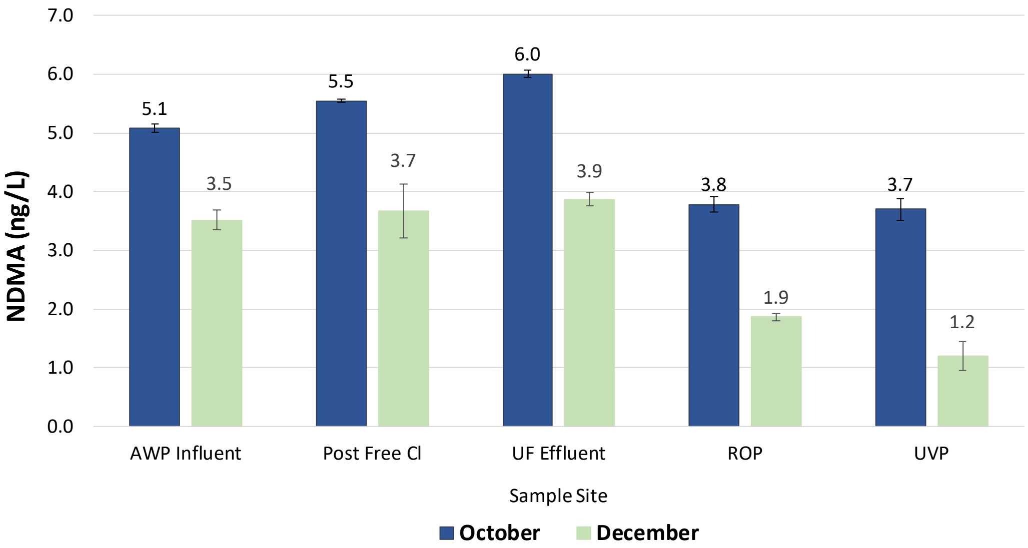


Figure 16. NDMA concentration in PDMWD Advanced Water Purification Demonstration Facility at each stage of treatment (October 16 and December 12, 2019)

The occurrence of NDMA precursors for the October 2019 sampling event at the PDMWD Advanced Water Purification Demonstration Facility is shown in Figure 17. NDMA precursor concentration was similar to but higher in the plant influent of the PDMWD facility compared to the OCWD AWPF by approximately 700 ng/L on this sampling day; this concentration likely varies over time and between sites as a function of local wastewater character. RO removed NDMA precursors by approximately 1280 ng/L or 99.6 percent, which was similar to the excellent RO performance shown at OCWD.

UV/HOCl (free chlorine) AOP slightly reduced the concentration of NDMA precursors (0.8 ng/L), but the removal was not always statistically significant. For example, there is a large degree of error in the duplicate analysis of the UV product water sample from December (Figure 17). Prior work by the project team at OCWD site indicated that UV-AOP removal of precursors is highly variable day to day, whether via free chlorine, chloramine, or H_2O_2 AOP (Hokanson et al. 2019; Roback et al. 2019)), varying from less than 10 percent to 100 percent (i.e., non-detectable precursors in product water). This may be due to inherent variability in the character (recalcitrance) of the pool of NDMA precursors (a mixture of many compounds) from day to day. Overall, this sampling event indicates again that NDMA precursors are not necessarily susceptible to UV-AOP and that RO is the core barrier to UV-AOP precursors. Due to the high level of variability, further work is required to understand whether a certain oxidant (e.g., free chlorine or H_2O_2 AOP) may be more consistently effective at destroying NDMA precursors and thus minimizing issues with NDMA rebound in finished water after UV-AOP at the plant NDMA compliance point or in the water delivery/distribution system.

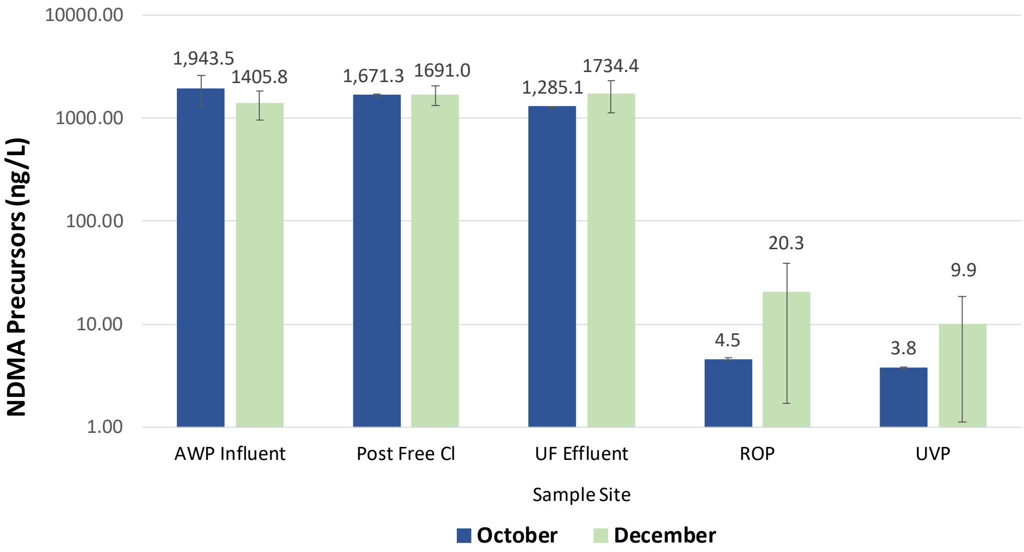


Figure 17. NDMA precursor concentration in PDMWD Advanced Water Purification Demonstration Facility at each stage of treatment (October 16 and December 12, 2019)

3.2.5 PDMWD Event 2 (December 2019)

Unlike in Event 1, the UV/AOP process at PDMWD in Event 2 was successful in removing NDMA to below the detection limit. This indicates that the UV/AOP process when utilizing free chlorine as the oxidant may be more variable than when using hydrogen peroxide. This was also the case when UV pilot testing with different oxidants was completed in Task 6. In this event, removal of NDMA precursors by RO was highly effective and removal by UV/AOP was approximately 50 percent. Contrasted to Event 4 at OCWD, the UV/AOP process can be seen to be highly variable for removal of NDMA precursors. This is also illustrated in the results from Task 6.

3.2.6 Excitation Emission Matrix Spectroscopy

Four components of EEMs were compared to NDMA precursor concentrations to determine whether any of the components were correlated to NDMA precursor concentration. At OCWD, precursors tended to be most correlated with tryptophan-like compounds suggesting the two may share some common characteristics and that this component could be a surrogate for NDMA precursors at this facility (Table 3). At PDMWD, precursors were most correlated with tryptophan-like and aromatic protein compounds suggesting more variability than at OCWD. Future work should be completed to further explore whether other EEMs metrics could be surrogates for NDMA precursors.

Table 3. Pearson correlation coefficients for NDMA precursors

Event	Pearson Correlation Coefficient			
	NDMA Precursors vs. Humic-like Compounds	NDMA Precursors vs. Aromatic Proteins	NDMA Precursors vs. Fulvic-like Compounds	NDMA Precursors vs. Tryptophan-like Compounds
OCWD Event 2	0.947	0.961	0.954	0.998
OCWD Event 4	0.788	0.787	0.780	0.808
PDMWD Event 1	0.956	0.966	0.959	0.994
PDMWD Event 2	0.872	0.992	0.990	0.945

3.3 Impact of Membrane Cleaning on NDMA and NDMA Precursor Removal

3.3.1 Baseline RO Removal of NDMA and NDMA Precursors

The RO system at the AWPF consists of 21 three-stage 5-MGD units that together produce up to 100 MGD (379 MLD) of RO permeate. The facility has a mixture of RO units with older and newer membranes (over the course of each membrane’s approximately 5- to 8-year membrane life) from different manufacturers. In order to better understand the typical rejection performance and potential range of rejection values for NDMA and NDMA precursors by RO, samples were collected from the RO feed and RO permeate of each of 20 RO units at the AWPF in November 2019. The samples were collected once in the morning and once in the afternoon on the same day and rejection of NDMA and NDMA precursors was calculated. This extremely high number of samples was enabled by the rapid, low-cost NDMA method under development that was described earlier in this report, allowing an unprecedented degree of NDMA/precursor rejection characterization across a real-world potable reuse facility. The sampling results for NDMA are shown in Figure 18 and for NDMA precursors in Figure 19.

NDMA rejection in the seven RO trains ranged from an average of 19 to 53 percent, typically averaging 40 to 50 percent. Each train contains three RO units, each of which contains 1,050 individual RO membranes (elements). Rejection averages in each of the trains were similar between the morning and afternoon sampling, except for in Train D, where one of the units (Unit 3) allowed for the passage of a higher concentration of NDMA in the afternoon. The reason is unknown and could be due to a small breach in one area of the unit, or to a heterogeneous NDMA peak in the RO feed water. Breaches can also occur in O-rings, via poor seals, and in places where the glue line edges of the membrane have become unsealed.

NDMA precursors were well removed both in the morning and afternoon sampling. Rejection percentage averages ranged from 97 to 99 percent. The large percent rejection is a function of both the efficiency of the RO process in removing NDMA precursors and the high concentration of NDMA precursors in the RO feed water (average of approximately 350 ng/L). Total NDMA precursor concentrations in the RO permeate ranged from 2.2 to 20.4 ng/L. This indicates that, depending on the efficiency of the UV-AOP process, the potential to form NDMA in the finished product water could be as high as 20.4 ng/L assuming no removal of precursors during UV-AOP, or even higher if precursors are transformed to more reactive forms. Prior studies by the project team have indicated that UV-AOP removal of NDMA precursors can be quite variable and sometimes fairly low (Hokanson et al. 2019; Roback et al. 2019).

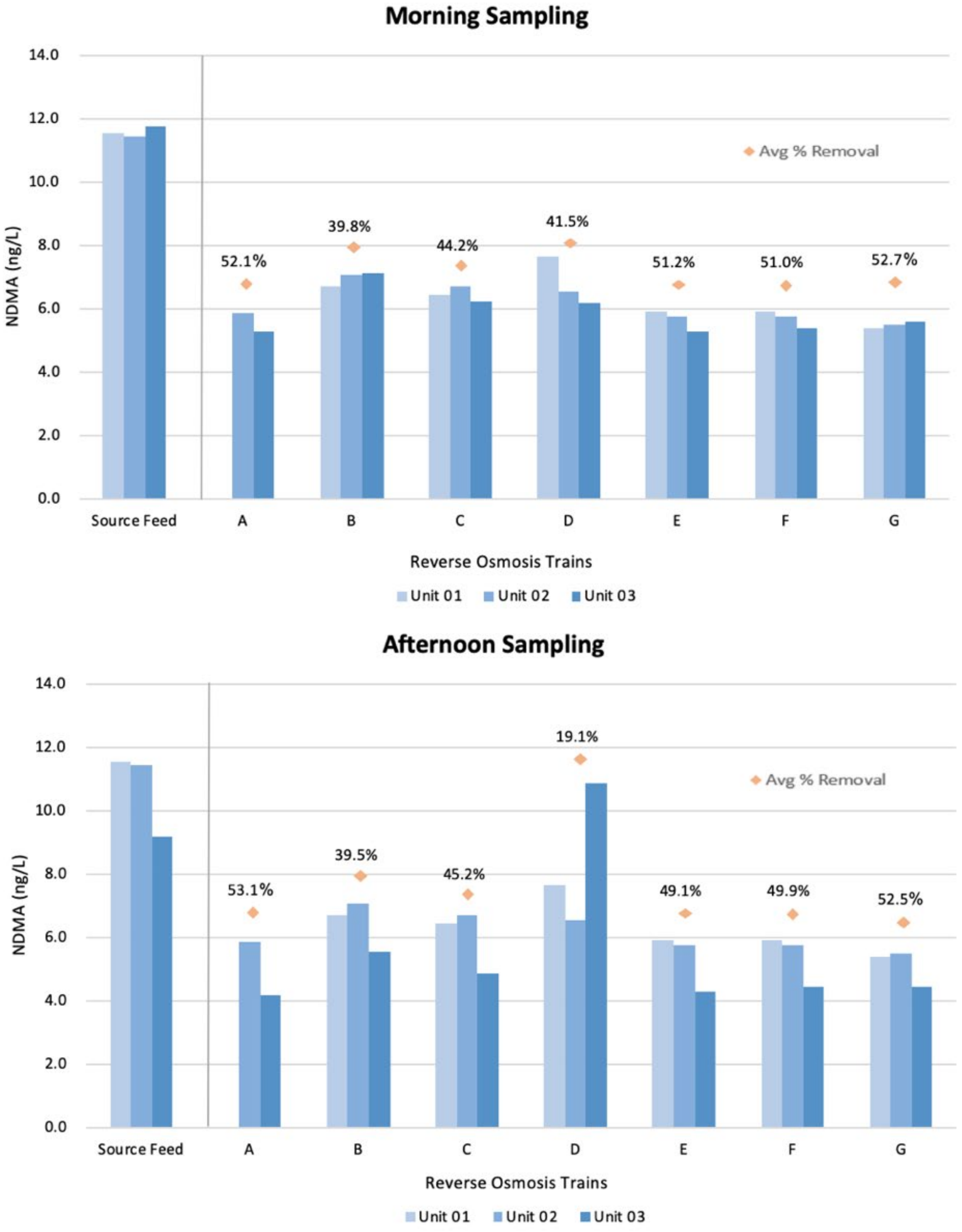


Figure 18. NDMA concentration in the RO feed water (source feed) and RO permeate from 20 membrane units in seven RO trains in the morning (top panel) and afternoon (bottom panel) on the same day

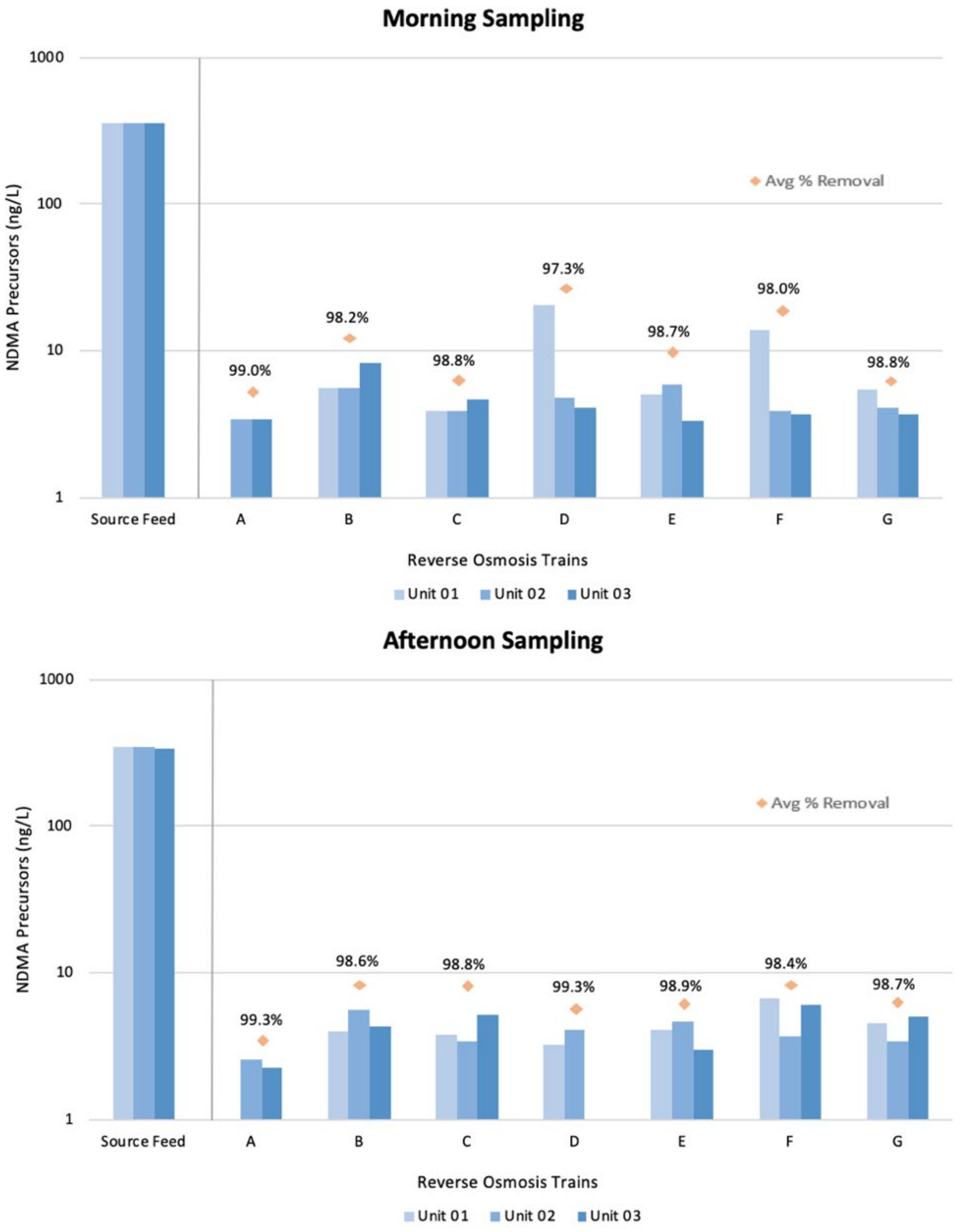


Figure 19. NDMA precursor concentration in the RO feed water (source feed) and RO permeate from 20 membrane units in seven RO trains in the morning (top panel) and afternoon (bottom panel) on the same day

3.3.2 Impact of Membrane Cleaning

In May 2018, OCWD operations staff completed a standard membrane cleaning for certain RO units. Grab samples were collected prior to the event to establish the baseline conditions immediately prior to the cleaning, and afterwards to assess cleaning impact (Event 1). Grab samples were collected from the RO feed and RO permeate of two membrane units containing ESPA2-LD Hydranautics membranes on 3 days at multiple times over 1 week prior to the membranes being cleaned. After the cleaning, 12 additional grab samples were collected from the RO feed and RO permeate over 4 weeks. Samples were collected at multiple time points on each sample day. In April 2019 (Event 2), samples were collected for 3 days prior to membrane cleaning in Unit A01 and 1 day prior in Unit A02. Samples were collected twice per week in the 2 weeks following the cleaning, and once per week for 2 weeks after that. NDMA and NDMA precursor percent rejection were calculated for each membrane unit.

3.3.2.1 Event 1 (May 2018) Evaluation of Units E02 and D01

For Unit E02, the sampling results pre- and post-cleaning are shown in Figure 20 (NDMA) and Figure 21 (NDMA precursors) for Unit E02. NDMA removal prior to membrane cleaning averaged 39 percent. That percentage average dropped to 23 percent the day following the cleaning. Rejection of NDMA continued to decline for 4 weeks post cleaning. Thus, rather than recovering over the 4-week period which is typically observed for general water quality (and NDMA) based on operator/industry experience, NDMA rejection continued to worsen following the cleaning.

Similar to NDMA rejection, NDMA precursor rejection (Figure 21) decreased immediately after the membrane cleaning (average rejection pre-cleaning was 98 percent, compared to average rejection one day post-cleaning of 60 percent). However, contrary to NDMA rejection, rejection of NDMA precursors rebounded to similar levels post-cleaning (average rejection after 10 days was 99 percent). This suggests that the mechanism responsible for removal of NDMA and removal of NDMA precursors is different and that the NDMA removal mechanism is more sensitive to membrane cleaning. NDMA rejection can also be increased in the presence of an adequate fouling layer. Removing this layer during membrane cleaning will decrease NDMA rejection.

For Unit D01, NDMA rejection declined after the membrane cleaning, similar to the NDMA rejection trend for Unit E02. Initial NDMA rejection was also lower in this membrane unit (average NDMA rejection pre-cleaning in Unit D01 was 16 percent, compared to average NDMA rejection pre-cleaning in Unit E02 of 39 percent). NDMA rejection also continued to decline during the 4-week monitoring period post cleaning, as it did in Unit E02. However, in the case of Unit D01, NDMA percent rejection became negative after 12 days (i.e., there was more NDMA in the RO permeate than the RO feed). This negative percent rejection trend increased in intensity over the 4-week period, with the final percent rejection after 4 weeks averaging -21 percent.

A negative rejection value indicates that the RO permeate concentration of NDMA is greater than the RO feed water concentration (paired grab samples were collected at the same time from feed and permeate throughout sampling program). This suggests that the membrane itself could be leaching NDMA or leaching NDMA precursors that are quickly reacting with the ambient chloramines to form NDMA, in increasing quantities post-cleaning. NDMA precursors have been shown in previous work to leach from nanofiltration membranes (Ersan et al. 2015). More research is needed to better understand the extent and nature of potential NDMA precursor leaching, including whether it is static or impacted by membrane cleaning, as well to better understand the mechanism of NDMA and NDMA precursor rejection by RO membranes.

Another possible explanation for the outcomes discussed above is that changes to the membrane during the cleaning process (addition of caustic and/or acid) causes some of the NDMA that has adsorbed to the membrane to desorb resulting in more NDMA in the ROP than ROF. This theory that NDMA may be desorbing from the membrane after membrane cleaning relies on the fact that NDMA rejection is governed by the principles of surface adsorption and internal adsorption, following the solution-diffusion model. However, Steinle-Darling et al. (2007) found that N-nitrosamines were likely not absorbed by the membrane matrix given experimental data, despite the theoretical possibility. Steinle-Darling et al. revealed a strong correlation between molecular weight of N-nitrosamines rejection by RO membranes, suggesting that steric hindrance may be a major rejection mechanism for N-nitrosamines (Steinle-Darling et al. 2007). Additionally, NDMA is very hydrophilic but most commercial RO membranes are classified as hydrophobic. Thus, hydrophobic interactions (e.g., adsorption) between NDMA and RO membranes should be minimal. This further underscores the idea that NDMA is rejected via pore size rather than adsorption.

If leaching of NDMA or NDMA precursors from the membranes occurs after a membrane cleaning, this would confound the observations regarding rejection, since a lower apparent rejection value could be due to either a true decrease in rejection or an otherwise increased permeate concentration from leaching. Differentiating rejection changes from leaching would require future work in controlled experiments.

Rejection of NDMA precursors by Unit D01 was similar to Unit E02. Precursor rejection decreased after the membrane was cleaned and then increased to similar levels as pre-cleaning. However, in the case of Unit D01, precursor removal did not remain steady at the pre-cleaning rate. The negative effect of membrane cleaning may therefore have lasted longer in this membrane unit and would have required longer term sampling to confirm a full return to pre-cleaning performance.

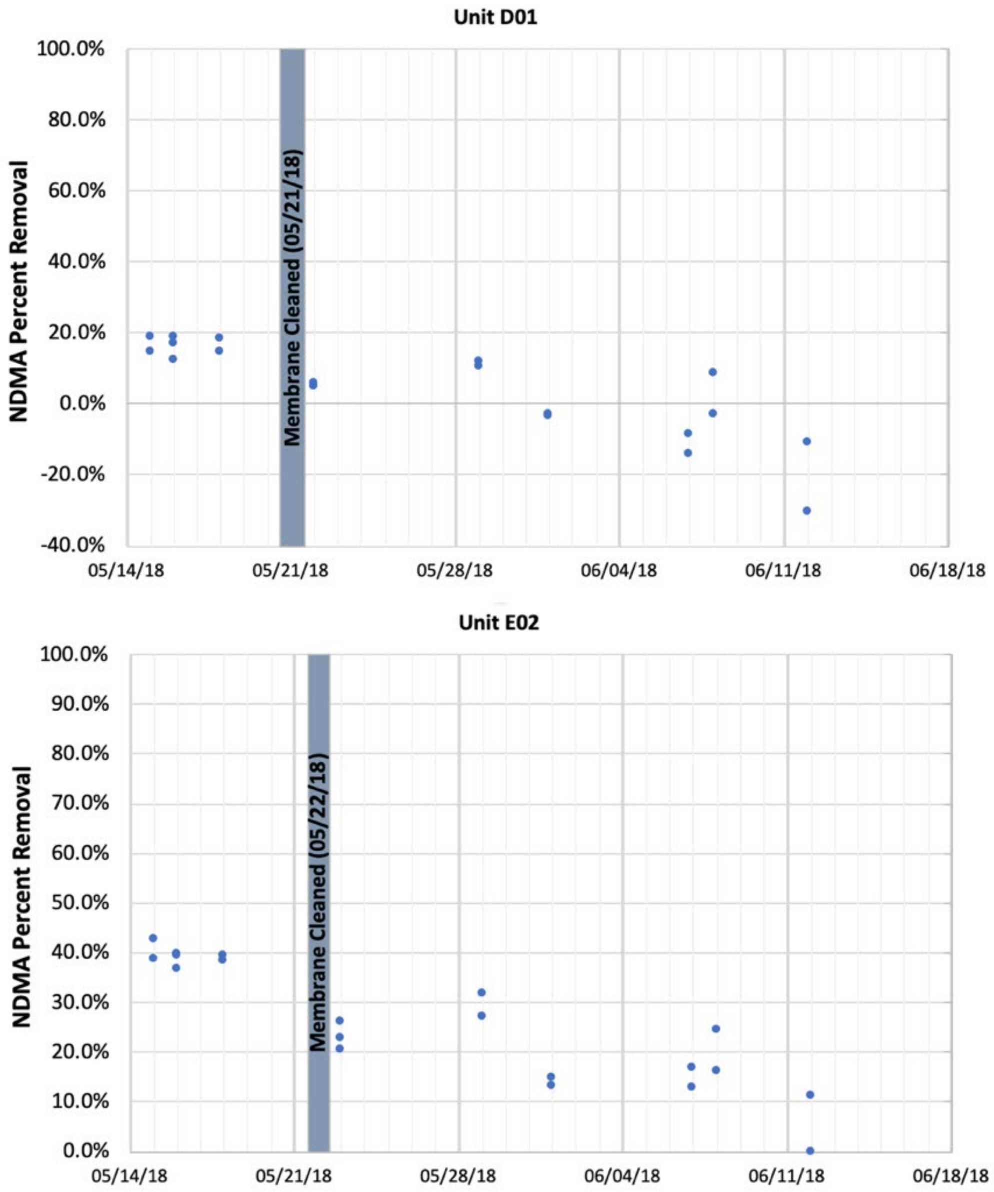


Figure 20. Event 1 (May 2018) NDMA percent rejection before and after membrane cleaning in Units D01 and E02

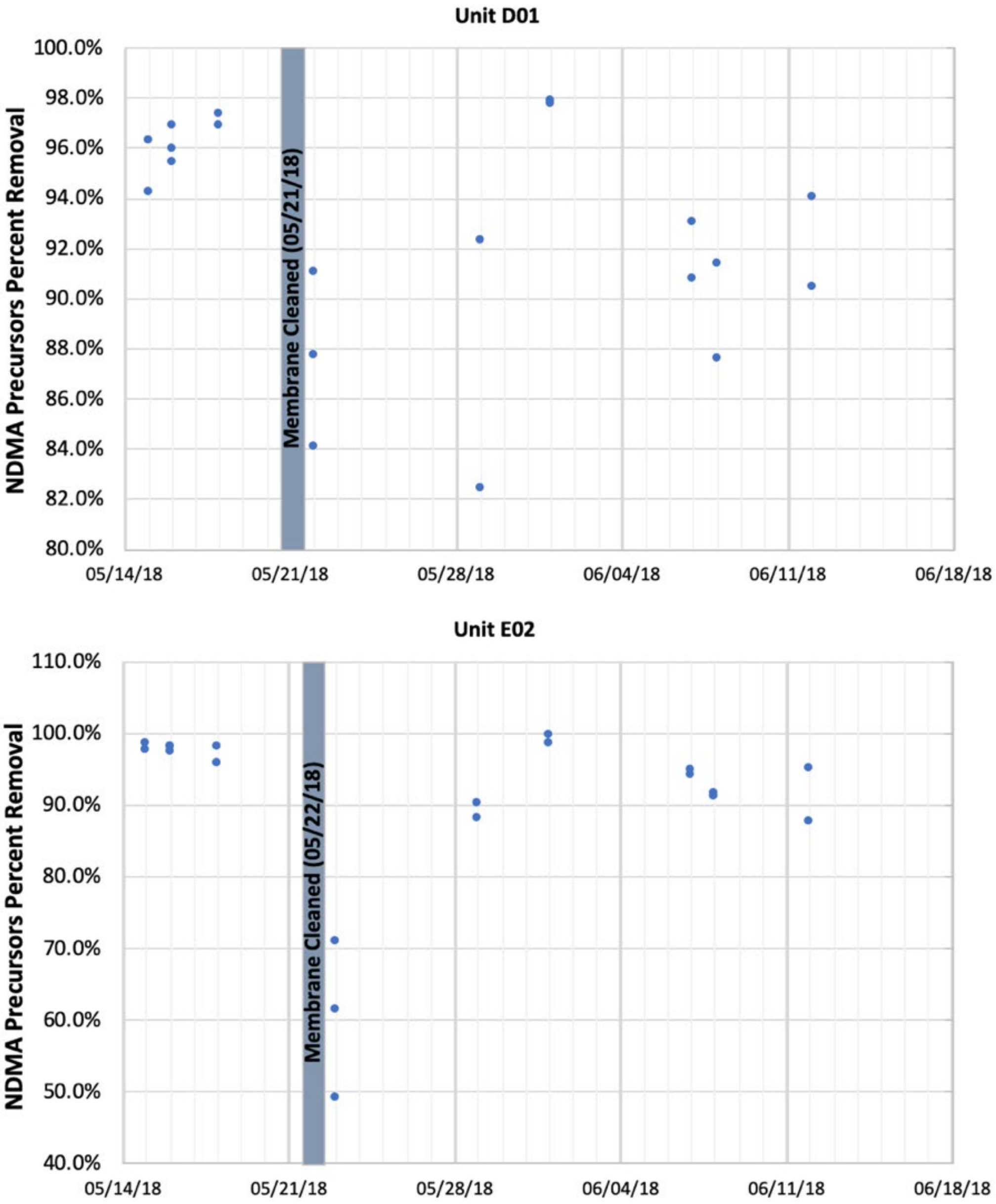


Figure 21. Event 1 (May 2018) NDMA precursor (FP) percent rejection before and after membrane cleaning in Units D01 and E02

3.3.2.2 Event 2 (November 2019) Evaluation of Units A01 and A02

In Event 2, an additional two RO units were sampled. In both units, NDMA rejection decreased after membrane cleaning and remained lower in the 4 weeks following the cleaning (Figure 22). In Unit A01, NDMA rejection decreased from an average of 61 percent to 54 percent after membrane cleaning. For Unit A02, the decrease was from 64 percent to 53 percent after membrane cleaning.

NDMA precursor rejection did not appear to decrease after membrane cleaning (Figure 23). Rejection of NDMA precursors averaged 98.6 percent to 98.5 percent in Unit A01 before and after cleaning, respectively, and 99.2 percent to 99.0 percent in Unit A02. A temporary decline in rejection of NDMA precursors was expected post-cleaning and was shown during Event 1 (see previous section) and was likely not observed in Event 2 due to a delay in the post-cleaning sample collection such that rejection had already rebounded.

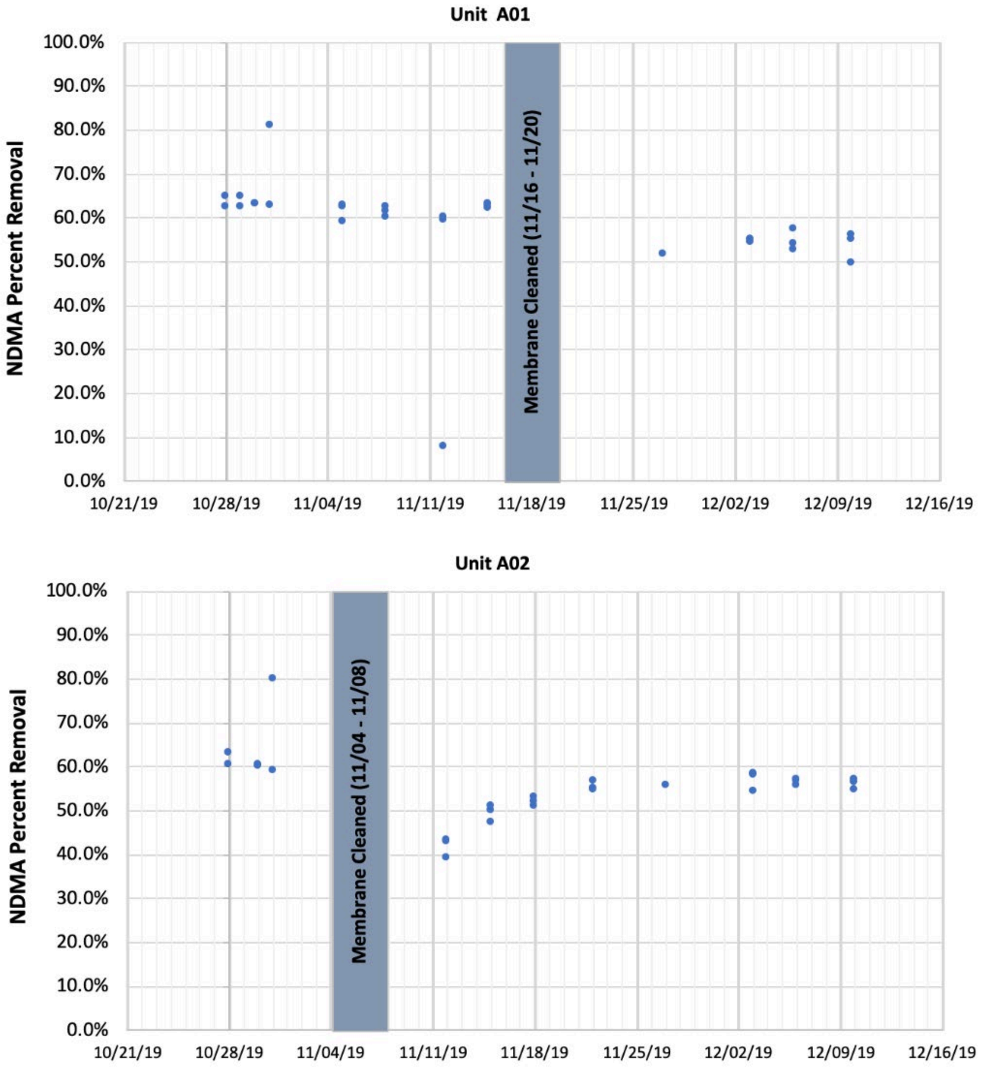


Figure 22. Event 2 (November 2019) NDMA percent rejection before and after membrane cleaning in Units A01 and A02

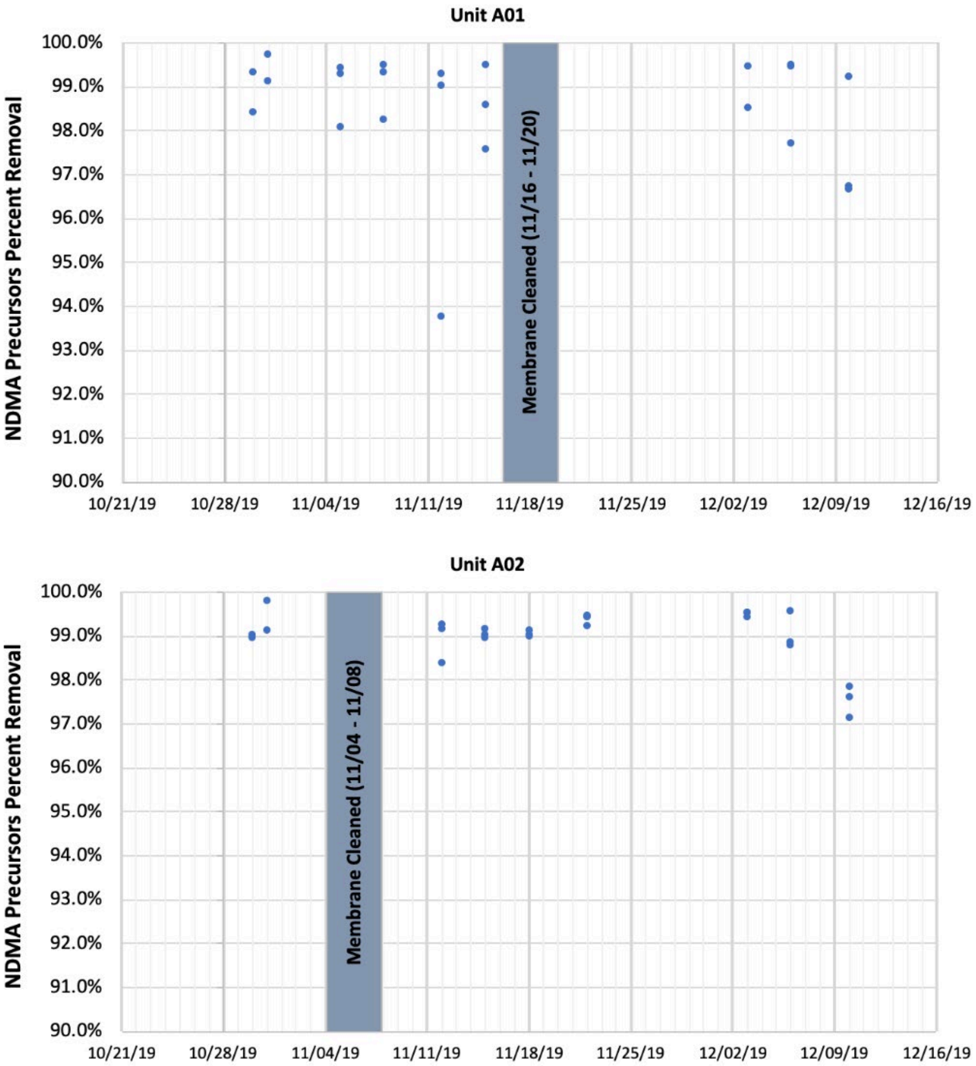


Figure 23. Event 2 (November 2019) NDMA precursor percent rejection before and after membrane cleaning in Units A01 and A02

In summary, RO membrane cleaning did not have a significant impact on the rejection of NDMA precursors, indicating that membrane cleaning damage is likely very minor or insignificant with respect to NDMA precursors. This finding may be membrane-specific for different manufacturer's membranes. The impact of cleaning on NDMA rejection was also measured but was not the focus of the study since RO is known to only partially remove NDMA; thus, the observed decline in NDMA rejection that was observed in this study after membrane cleaning is not as important from the perspective of NDMA compliance. This is because the subsequent UV-AOP step can be relied upon to remove NDMA.

Additionally, this work introduced larger questions about the mechanism of NDMA rejection by RO, which is not well understood.

3.4 Contribution of NDMA to Treated Water from Treatment Plant Chemicals

All samples of treatment plant chemicals from the OCWD AWPF had background N-nitrosamine concentrations at or below the Milli-Q blank (2 ng/L). The Milli-Q blank was higher than expected for NDMA and NDBA (11 and 4.4 ng/L, respectively). This has been observed previously in specific instances and is presumed to be associated with leaching of N-nitrosamine precursors from the resin contained in the laboratory Milli-Q system, which has been observed by other labs with similar systems. Considering possible low-level contamination of the Milli-Q water and the dilution factors here, reported values were limited to 0.55 and 0.22 ng/L for NDMA and NDBA, respectively. Although the blank was greater in concentration than anticipated, this is a reasonable reporting limit considering the N-nitrosamine concentrations observed in the treatment plant water were considerably higher.

Results were translated from FP test dilutions to likely in-plant dilutions of 10,000-fold. Except for NPIP from the Clarifloc polymer, the contribution to N-nitrosamine formation from AWPF chemical additions is extremely low (see Table 4; only formation greater than the blank is shown). Thus, the chemical additions to advanced treated water tested here would each be expected to contribute less than 1 ng/L of N-nitrosamines to the finished water.

Table 4. Potential *N*-nitrosamine formation from AWPF chemical additions based on 10,000x dilution of stock solutions into the plant flow

AWPF Chemical Addition	NDMA FP (ng/L)	NMEA FP (ng/L)	NDEA FP (ng/L)	NDPA FP (ng/L)	NDBA FP (ng/L)	NPIP FP (ng/L)	NPYR FP (ng/L)	NMOR FP (ng/L)
Antiscalant	0.1	0.1	0.1	0.1	0.5 ± 0.06[a]	0.1	0.1	0.1
Clarifloc A210P polymer	0.1	0.1	0.1	0.1	0.1	4.3	0.1	0.1
Citric acid	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Lime supernatant	0.8 ± 0.1	0.1	0.1	0.1	0.24 ± 0.04	0.1	0.1	0.1
Memclean	0.1	0.1	0.1	0.7 ± 0.1	0.1	0.1	0.1	0.1
H_2O_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
93% H_2SO_4	0.1	0.1	0.03	0.1	0.1	0.1	0.1	0.1
50% NaOH	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Shaded (gray) data cells indicate values based on the MDL

a-Error is based on the range of deviation from the mean of duplicates.

Clarifloc polymer is included in the lime slurry that is added to the UV-AOP product water at the plant to increase the pH to avoid corrosion in piping networks. Significantly less polymer is added to the lime slurry than was tested here and the polymer in the plant only partially carries over to the finished product water. Therefore, N-nitrosamine formation due to this polymer at AWPF is expected to be quite low. Considering the likely dilutions of all of these compounds, chemical additions to the source waters throughout the AWPF are unlikely to significantly contribute to N-nitrosamine formation.

3.5 Impact of UV-AOP Scenarios on NDMA Precursors and Unidentified Trace Organics

Pilot-scale testing of UV-AOP was completed at OCWD using AWPF facility water (RO permeate) to determine the impact of the oxidant choice for UV-AOP [H_2O_2, free chlorine (HOCl) and residual or supplemental chloramines (NH_2Cl)] on the transformation of NDMA precursors and other trace organics. A series of pilot UV-AOP tests was completed in August 2018 (Event 1). A similar set of tests was repeated one year later (Event 2) for the purpose of duplication.

Though the focus of the overall study is NDMA and NDMA precursors, the use of non-target analysis methods (both LC-based and GC-based) to examine the water quality performance of UV-AOP allowed the investigation to be broadened to other trace organics that are detectable with these methods. This section describes the results for NDMA and NDMA precursors (measured by HPLC-PR-CL, i.e., target analysis) and other wastewater-derived, trace-level organics (estimated by non-target analysis).

3.5.1 NDMA and NDMA Precursors

NDMA precursors were measured using a Uniform Formation Conditions (UFC) test. Similar to the FP test, the water sample in the UFC test is dosed with monochloramine at pH 8 and allowed to react for 3 days in the dark at room temperature. However, in the FP test, the dose of monochloramine is 18 mg/L as Cl_2 while in the UFC test, the dose is 5 mg/L as Cl_2. This is similar to the monochloramine residual concentration found in the UV-AOP product water at OCWD and thus was used to be more representative of the dose in the final product water and measure realistic formation of NDMA from precursors. Due to the challenge of working with very low NDMA/precursor concentrations yet trying to demonstrate any difference in their removal owing to treatment conditions, UFC tests were duplicated for each sample in addition to duplicate NDMA analysis for all samples.

In Event 1, the resulting concentrations of oxidants measured after dosing were 2.9 mg/L for hydrogen peroxide, 3.4 mg/L as Cl_2 for supplemental monochloramine, and 2.0 mg/L as Cl_2 for free chlorine. In the "no oxidant addition" scenario (i.e., UV/residual chloramine scenario), the background total chlorine concentration was 2.3 mg/L as Cl_2. In Event 2, the concentrations were 3.0 mg/L H_2O_2 and 2.0 mg/L as Cl_2 for free chlorine. During Events 1 and 2, RO permeate (ROP) was collected prior to oxidant dosing, in addition to collection of UV-AOP feed and product, in order to determine whether the oxidant itself was responsible for destruction of

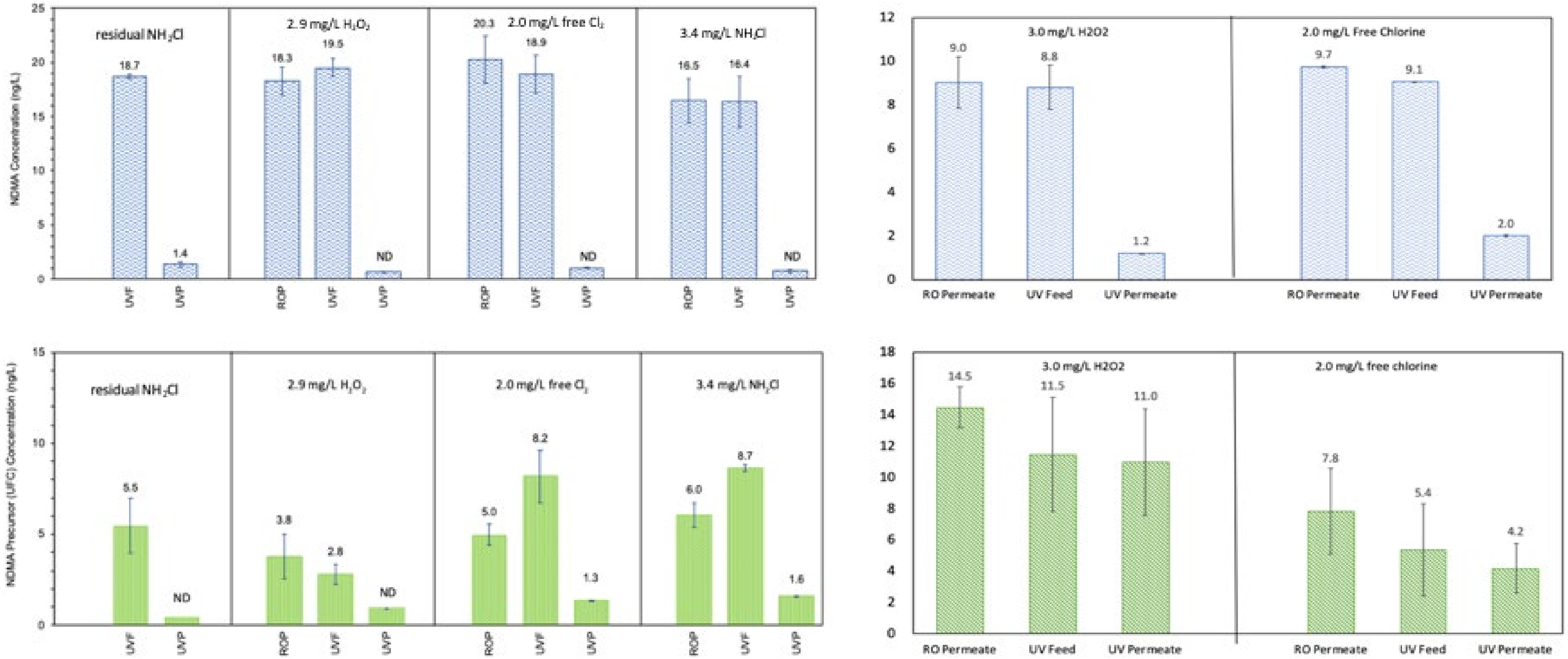
NDMA precursors (i.e., before UV-AOP). These pilot sampling sites are herein referred to as ROP (no oxidant added), UVF (UV-AOP feed water which is ROP with oxidant added), and UVP (UV-AOP product water).

The results for NDMA and NDMA precursors are shown in Figure 24. For both Events 1 and 2, NDMA was removed to below or very near the detection limit by all UV-oxidant conditions. This is not surprising since it is the UV light that is responsible for NDMA destruction (due to NDMA's photosensitivity) irrespective of the oxidant used. Of note is the observation that the addition of free chlorine or chloramine, which can react with precursors to form NDMA, did not result in a significant increase in NDMA comparing the ROP to UVF sampling sites.

The results for NDMA precursors were more variable. In Event 1, the addition of 2.9 mg/L of hydrogen peroxide to RO permeate (UV-AOP influent) in the absence of UV light may have removed some (approximately 26 percent) of the NDMA precursors (i.e., prior to UV-AOP), but due to the large standard deviation of the NDMA measurements, this decrease is not statistically significant. The application of UV to this source water removed the remainder of the precursors to below the detection limit.

Both the addition of NaOCl (for UV/free chlorine, i.e., UV/HOCl) and preformed monochloramine to the ROP resulted in an increase in NDMA precursors, suggesting formation of precursors by these chlorinated oxidants (i.e., oxidation of background organics resulting in increased NDMA formation potential of the organics). However, NDMA precursors were subsequently well removed by both under UV-AOP conditions, such that product water concentration of precursors was still very low despite this formation. In this test, NDMA precursors were also well removed by UV alone (no added oxidant; background chloramines are present). It is also possible that the increase in NDMA precursors after NaOCl and NH_2Cl addition is an artifact of the UFC test. The addition of both preformed monochloramine and NaOCl resulted in increased concentrations of dichloramine. Although the concentration of monochloramine is standardized for the UFC test, in the UV/HOCl and the UV/NH_2Cl samples, the increased concentrations of dichloramine may have resulted in increased NDMA formation. Future work is needed to determine the effect of oxidant dosing independently.

In Event 2, NDMA and NDMA precursor removal was evaluated for UV-AOP using a subset of the oxidants evaluated in the prior event: UV/H_2O_2 and UV/HOCl. This reduction in treatment scenarios allowed increased sampling for non-target analysis (see results in next section) to include the ROP (pre-oxidant) site.



Conditions: "None" = no *additional* oxidant was dosed into the UV-AOP pilot feed water (i.e., UV alone), but residual chloramines are present due to upstream use for plant membrane biofouling control; oxidant doses were 2.9 mg/L hydrogen peroxide, 2.0 mg/L as Cl_2 free chlorine, and 3.4 mg/L as Cl_2 monochloramine. Error bars indicate the standard deviation for duplicate (n = 2) samples (for NDMA) or the standard deviation for duplicate NDMA samples from duplicate UFC tests (n=4) to determine FP (for NDMA precursors)

Figure 24. Event 1 in 2018 (left two panels) and Event 2 in 2019 (right two panels) removal of NDMA and NDMA precursors for UV/residual NH_2Cl, UV/H_2O_2, UV/HOCl, and UV/supplemental NH_2Cl

Similar to Event 1, NDMA was removed to below the detection limit by UV/HOCl (from NaOCl dosing) and UV/H_2O_2. However, NDMA precursors (UFC) were not removed by UV/HOCl or UV/H_2O_2 with statistical significance. In other words, while in Event 1 the NDMA precursors were removed to below or near the detection limit for all oxidant conditions, in Event 2 there was not a statistically significant difference in precursor concentration among ROP, UVF, and UVP sites. This may be attributed to: 1) actual performance difference between Event 1 and 2, dependent on the precursor type present in the water which can vary from day-to-day; and 2) analytical challenges of demonstrating removal with statistical significance for trace organics that are already extremely low in concentration in the feed water and thus only slightly lower (if at all lower) in the product water after treatment. Overall, the findings suggest that UV-AOP with various oxidants can remove some portion of the NDMA precursor pool but the efficacy will be variable day to day. With respect to the effect of the oxidant itself (i.e., ROP compared to UVF), NDMA precursors concentration was not significantly different before and after oxidant addition for H_2O_2 and HOCl in Event 2, suggesting little impact of oxidation alone on net precursor reduction; this was similar in Event 1 except that dosing with NaOCl may have slightly increased the NDMA precursor concentration as discussed above (i.e., activating the organics to more formation potential).

3.5.2 Non-Target Compounds

Samples were collected from the above described UV/AOP pilot tests during Events 1 and 2 to assess the formation and destruction of previously unidentified compounds. Samples were shipped for SPE and non-target analysis to UNR, UCB, and/or SDSU.

UNR conducted sample extraction using either a method for isolating NDMA precursor compounds (MCX SPE cartridge; Event 1 and 2) or a general extraction for a variety of compounds (HLB SPE cartridge; Event 2 only) and sent the samples to UCB for analysis using LC-qTOF-MS (previously described in Section 2.6.1). This analysis determines the occurrence of more hydrophilic compounds that can be determined by liquid chromatography (LC). SDSU conducted sample extraction using a general extraction method to isolate a variety of compounds in both events and then analyzed the compounds using GC×GC/TOF-MS (previously described in Section 2.6). This analysis by gas chromatography (GC) generally determines more hydrophobic compounds. The combination of both GC and LC-based techniques allowed for a thorough exploration of previously unidentified compounds and how their destruction or formation differs when using different UV-AOPs (UV/HOCl, UV/H_2O_2, and UV/NH_2Cl). In order to accommodate the increased sample load due to extraction of samples with the HLB cartridge and MCX cartridge, the UV/supplemental NH_2Cl condition was eliminated from Event 2.

As one approach for analyzing the very large datasets produced by non-target analysis, for this project the total number of detected compounds (considered detected based on qualification by certain criteria, e.g., signal to noise ratio) were summed for each sample, and removal (and formation) of total number of compounds was compared between different UV-AOP conditions.

Thus, this analysis focuses on compound count rather than concentration. In water treatment, removal is more classically determined by calculating the reduction in concentration. For non-target analysis, concentration can be estimated separately via total peak area prior to any confirmation testing using authentic standards. Upon confirmation, which was not performed in this study, concentration can be more accurately determined.

3.5.2.1 NTA by SPE-LC/qTOF-MS

The library match screening performed on the mass chromatographs of the extracts from the MCX (NDMA precursor extraction) and HLB (general extraction) cartridges revealed the presence of several tentatively-identified compounds in RO permeate, UV-AOP feed water (RO permeate after oxidant addition), and UV-AOP product water. Results are summarized below for Event 1 and Event 2. Atenolol, DEET, lamotrigine, metoprolol, sucralose, benzotriazole, and 4- and 5-methyl benzotriazoles were the most prevalent compounds detected across both event sampling dates. UV/H_2O_2 and UV/HOCl performed similarly in reducing the measured peak area of the library matched compounds and better than supplemental NH_2Cl when used as an oxidant for UV-AOP.

Event 1

The UV/HOCl AOP effectively removed 99 percent of the total peak area (total amount of ionizable organics) from RO permeate, followed by UV/H_2O_2 at 98 percent. For UV/supplemental NH_2Cl, 61 percent of the total peak area for all compounds was removed, compared to 65 percent by UV/residual NH_2Cl (i.e., UV with no added oxidant). Thus, overall the use of H_2O_2 or HOCl as an AOP oxidant was far superior to chloramine as measured holistically by non-target analysis (i.e., based on summing total peak area as an estimate of concentration for hundreds if not thousands of compounds).

The four detected compounds (tentatively identified, i.e., not confirmed with authentic standards) occurring at the highest likely concentration were benzotriazole, the two isomers of methylbenzotriazole, and phthalic acid (Figure 25). The three benzotriazole compounds are anticorrosion agents in wastewater treatment and phthalic acid is a plasticizer. The three benzotriazole compounds were removed by the UV-AOP and not detected in the UV product water. The removal of these compounds was measured under each of the four UV oxidant conditions, in particular HOCl and H_2O_2, and to a lesser extent with supplemental NH_2Cl and residual NH_2Cl. Phthalic acid increased in peak area during UV/NH_2Cl (i.e. comparing UVF and UVP), suggesting that it may have been added during that treatment process or may be a transformation product of another compound that is oxidized during UV-AOP.

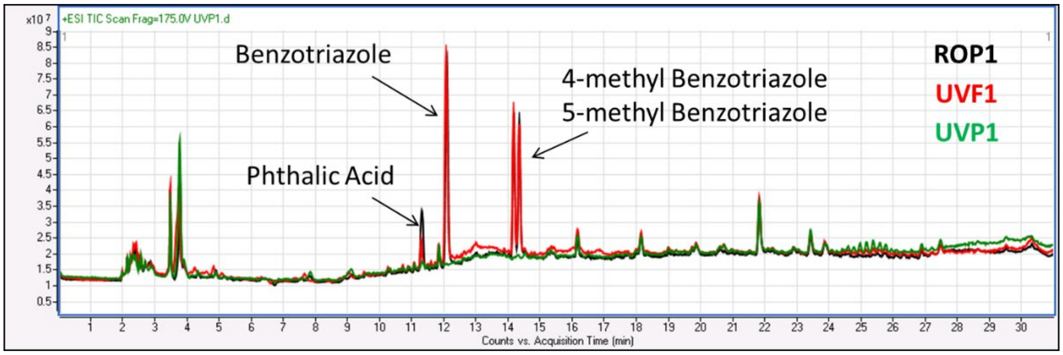


Figure 25. Example chromatogram from the UV/HOCl pilot test. The chromatogram shows large peaks of tentatively identified phthalic acid, benzotriazole, and the two isomers of methyl benzotriazole in RO permeate ("ROP1") and UV-AOP feed water ("UVF1"), which are absent in UV-AOP product water ("UVP1").

In terms of molecular weight, UV/HOCl, supplemental NH_2Cl, and H_2O_2 tended to produce molecules with slightly increased median mass (*m/z*) when compared to the RO permeate samples, suggesting photopolymerization of some compounds during these UV-AOPs. UV/residual NH_2Cl appeared to decrease median molecular weight. Notably, H_2O_2 initially decreased median molecular weight prior to UV, but then increased to greater than the median in the UV product sample. This is potentially due to initial oxidation of organic molecules by H_2O_2, followed by photopolymerization in the UV system. It is not clear at this time why this would be pronounced for samples treated with H_2O_2 but not for samples treated with other oxidants. However, these various shifts in mass were small and require further data analysis to evaluate statistical significance. Small shifts in organic-N content were also observed: UV/HOCl, UV/supplemental NH_2Cl, and UV/H_2O_2 oxidation conditions tended to produce molecules that were depleted (on a median basis) in organic N compared to the ROP samples. Overall, these changes are extremely small and are potentially not statistically significant, but the trends tend to follow those of NDMA formation potential across the treatment train.

The results based on total number of compounds detected by non-target analysis for Event 1 are shown in Figure 26. Application of UV/HOCl AOP to the RO permeate resulted in the formation of the least number (1,266) of identifiable new compounds (i.e., photolytic and oxidative by-products), while UV/NH_2Cl and UV/H_2O_2 resulted in similar numbers (2,280 and 2,167, respectively). Note that this analysis, based on counting compounds, does not account for changes in concentration; rather, it only accounts for qualified detections or lack of detections. The UV/HOCl, UV/ NH_2Cl and UV/H_2O_2 AOPs removed a similar number of compounds (2,306, 2,636, and 2,687, respectively). These data suggest that all of the evaluated AOPs remove more compounds than they produce; however, the production of new products is substantial. Whether or not these pose a risk will largely depend on their concentration, which is expected to be extremely low.

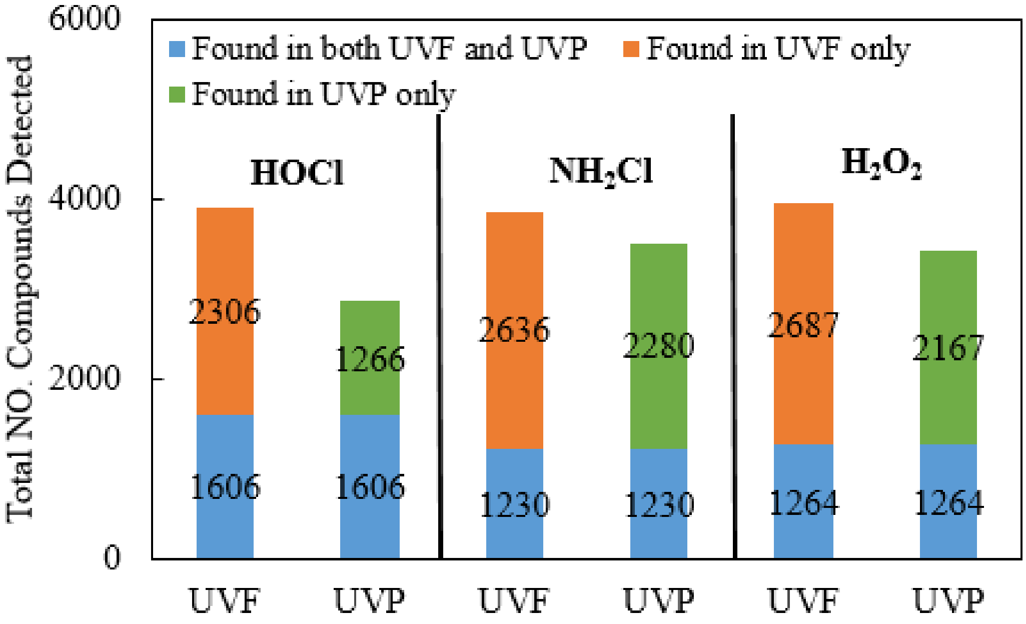


Figure 26. Total number of compounds detected by SPE-LC/qTOF-MS before and after UV-AOP for three different oxidants in Event 1. Orange bars represent compounds that were detected only in UV feed (i.e., removed by UV-AOP), green bars represent compounds if found only in the UV product water (i.e., transformation products), and blue bars represent compounds that were not completely removed (though they may have been reduced in concentration).

An important finding from this research, demonstrated in the next section discussing the GC-based results, was that the pre-oxidant (i.e., RO permeate) sample should be measured as well to more accurately compare different oxidants used in AOP. This is important because the oxidant itself can reduce or increase compound number prior to UV-AOP. Therefore, the net accounting (and thus oxidant comparison) should arguably be done by comparing RO permeate to UV-AOP product, as opposed to solely comparing UV feed to UV product.

Event 2

In Event 2, the trends in number of compounds, organic-N content, and median mass between the extracts from the MCX and HLB cartridges tend to be opposing. This is due to the fact that the cartridges are designed to extract slightly different types of compounds. However, when the MCX extracts were compared between Event 1 and Event 2, certain trends were also opposing. For example, the UV/H_2O_2 process in Event 2 produced fewer new compounds than UV/HOCl, which produced the lowest number of new compounds in Event 1 (Figure 26). This may be attributed to the fact that the compounds present in the feed water to UV-AOP at any given time differs, which would likely impact the trends and degree of removal by AOP processes for the pool of trace organic compounds.

Under all treatment conditions (HOCl and H_2O_2) for extraction with the MCX resin cartridge, removal of the total peak area (related to concentration) across all the detected compounds was

≥99.6 percent from RO permeate to UV product water. Changes across UV feed to UV product were nearly the same as RO permeate to UV product water, suggesting that the majority of removal during UV-AOP is attributable to UV-AOP removal as opposed to the oxidant addition itself (i.e., RO permeate to UV feed). Similarly, when organic matter was extracted with the HLB resin, peak area decreased by ≥98.6 percent based on comparing UV feed to UV product (no associated RO permeate sample was taken and extracted using the HLB extraction method).

Benzotriazole and the two methylated isomers present in Event 1 were also present with the greatest peak areas in Event 2, but all three were well removed by the UV-AOP process independent of oxidant.

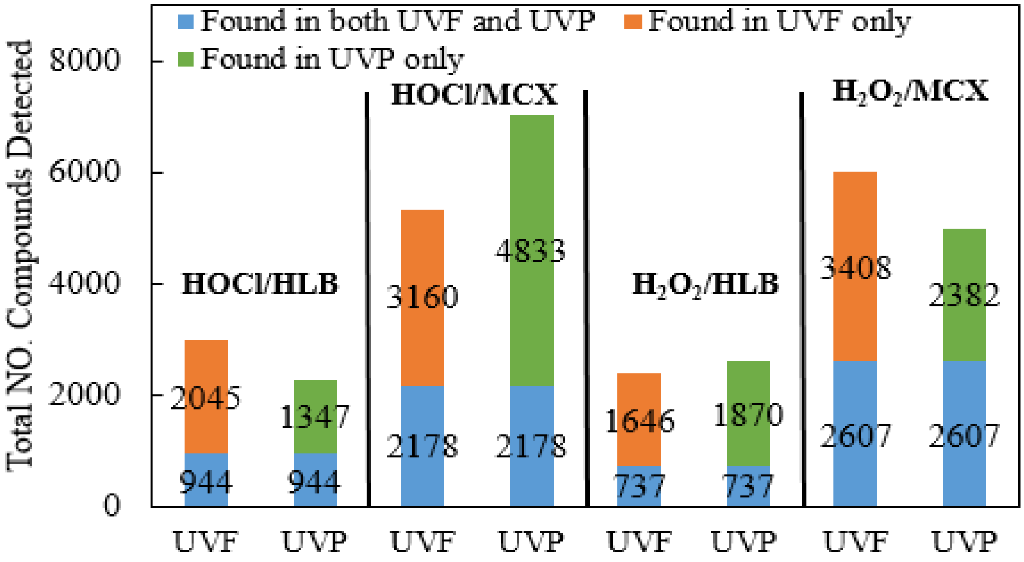


Figure 27. Total number of compounds before and after UV-AOP for three different oxidants in Event 2. Orange bars represent compounds that were detected only in UV feed (i.e., removed by UV-AOP), green bars represent compounds if found only in the UV product water (i.e., transformation products), while blue bars represent compounds that were not completely removed (though they may have been reduced in concentration).

For Event 2, as shown in Figure 27, the UV/HOCl AOP exhibited a greater number of total compounds formed through the process (green bars) compared to UV/H_2O_2 (6,180 v. 4,252 based on sum of HLB and MCX). In both cases, the MCX cartridge yielded the greatest number of UV-AOP byproducts. However, this is likely due to the differing extraction factors (1,000-fold for HLB and 2,000-fold for MCX), which were intended to mitigate breakthrough of polar analytes on HLB resin and likely decreased the number of some low concentration analytes in the extract. Thus, absolute numbers of compounds present in the UV product water should be used to compare treatment processes rather than indicate the quantitative compound presence due to the influence of extraction factors on the total number of compounds detected. In contrast to Event 1, the UV/HOCl process removed a similar number of compounds to the UV/H_2O_2 process

(5,205 v. 5,054), underscoring the impact of variable water quality containing a differing number and type of compounds on treatment efficiency.

3.5.2.2 NTA by SPE-GC×GC/TOF-MS

The library match screening performed on the GC×GC/TOF-MS mass chromatographs of the extracts from the HLB SPE cartridges revealed the presence of several tentatively identified compounds in RO permeate, UV-AOP feed water (RO permeate after oxidant addition), and UV-AOP product water. Results are summarized below for Event 1 and Event 2.

Event 1

In Event 1, samples were collected from the UV-AOP feed and product water of the UV pilot reactor (for this event, samples of RO permeate were not collected, i.e., samples prior to oxidant dosing). Results describing the total number of qualified compounds in the UV-AOP pilot feed and product water using non-target analysis by GC×GC/TOF-MS from Event 1 are shown in Figure 28 below. Similar to the LC-based method, in Event 2, UV/HOCl formed the greatest number of new compounds through UV/AOP, followed closely by UV/H_2O_2. UV/H_2O_2 and UV/supplemental NH_2Cl removed the greatest number of compounds (see percent removal values indicated in Figure 28) followed by UV/HOCl and UV with residual chloramines. The total number of qualified compounds in the UV-AOP pilot feed water (RO permeate plus an oxidant) ranged from 91 to 104, while the total number of qualified compounds found in the product waters ranged from 38 to 81, indicating an overall reduction in the number of compounds regardless of the operating condition. Transformation compounds (i.e., compounds unique to the product water absent in the feed waters) were found to be present in the product waters under all four AOP operating conditions, with the least number associated with UV/NH_2Cl (supplemental or residual).

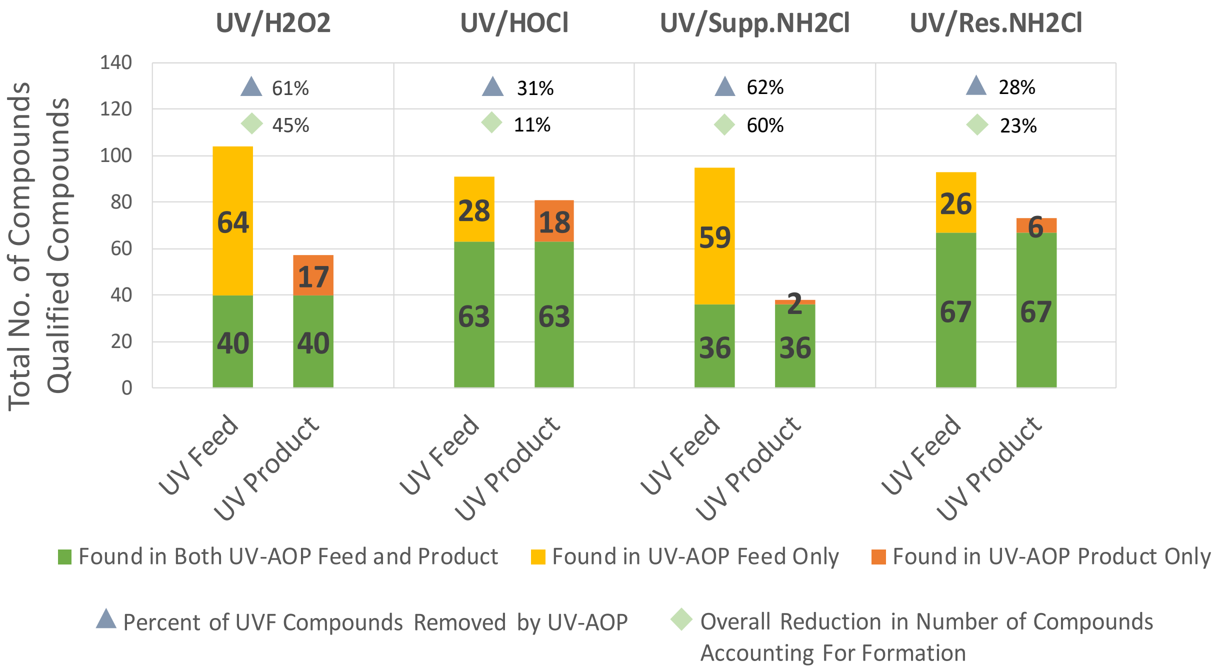


Figure 28. Event 1 removal and formation of qualified compounds determined by GC×GC/TOF-MS v. type of oxidant during pilot UV/AOP test

Event 2

As shown in Figure 29, pilot UV-AOP testing was repeated in Event 2 but for a subset of the previous oxidants (UV/H_2O_2 and UV/HOCl) and including an additional sampling site (the RO permeate i.e., UV-AOP pilot feed water prior to oxidant addition).

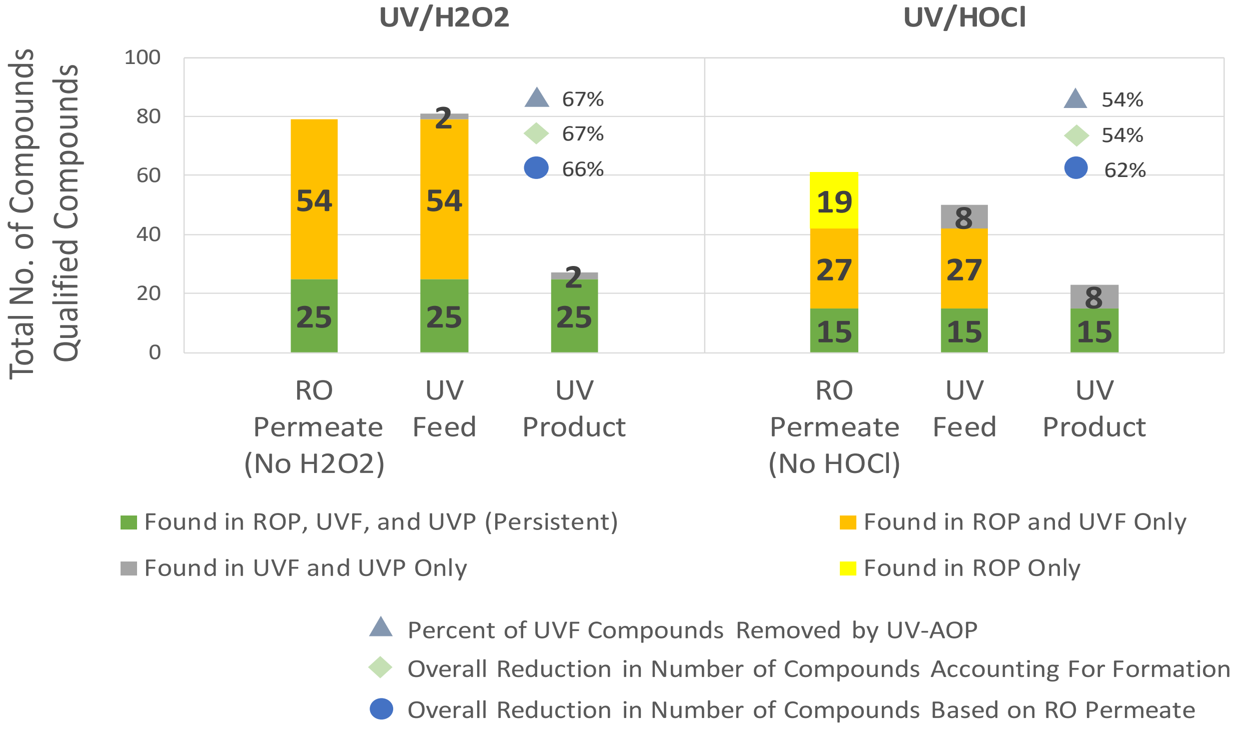


Figure 29. Event 2 removal and formation of qualified compounds determined by GC×GC/TOF-MS v. type of oxidant during pilot UV/AOP test

In Event 2, there were no UV-AOP transformation products identified. This is unexpected; thus, the mass spectra will be re-analyzed prior to journal publication. For the UV/HOCl system, there were 19 compounds that were removed after oxidant addition prior to UV-AOP, and 27 compounds removed by UV-AOP. There were also eight compounds formed by oxidant addition that were not subsequently removed by UV-AOP. Under the UV/H_2O_2 system, no compounds were removed by the addition of H_2O_2 alone, while 2 were created, and 54 compounds were removed by UV-AOP.

3.6 Conclusions

By examining the occurrence of NDMA, NDMA precursors, DBPs, and non-target compounds, this project illustrates the variability in types of trace-level, organic compounds (TOrCs) that are treated in advanced water purification plants to produce water acceptable for potable water reuse. Overall, RO treatment is known to be highly effective at removing (rejecting) a range of diverse compounds, and in this study was found to remove NDMA precursors to a very high degree which aids in reducing the level of NDMA rebound that may be observed in the final product water. However, the final treatment step, UV-AOP, was shown to only partially remove NDMA precursors from the finished water due to the recalcitrance of NDMA precursors to various types of AOP oxidants.

Each project task provided new information on the nature of organic compound treatment in advanced water purification facilities. The major conclusions for each task are outlined below:

1. High frequency monitoring of NDMA during advanced treatment (Section 3.1)
    a. Both NDMA and NDMA precursor concentrations are variable in AWPF influent. Concentrations typically propagate through the various stages of treatment. NDMA concentration appeared to slightly decline on the weekends compared to the weekdays.
    b. NDMA only exceeded the 10 ng/L monitoring trigger level in the finished product water on two occasions despite the large increase in frequency of NDMA samples measured in this study compared to typical weekly compliance monitoring.
    c. NDMA concentration may vary with chlorine concentration, but this is not always the case. This indicates that chlorine is an influencing factor; however, other factors (such as NDMA precursor loading) also play a role in NDMA occurrence.
    d. Other DBP (THM and HAA) concentrations also varied throughout the day. However, concentrations remained an order of magnitude lower than EPA MCLs for drinking water.
    e. While UV_{254} and TOC can be useful surrogates for the general organic character of waters, neither was correlated to the presence of NDMA or NDMA precursors, indicating that they cannot be used as tools to estimate NDMA or NDMA precursor loading and removal.
    f. EEMs components also varied over the course of the day and week, suggesting organic matter of multiple types is present at differing concentrations at different times in advanced water treatment plants, underscoring the variable nature of the source water quality.
2. NDMA precursor occurrence and fate in advanced treatment facilities from full-scale facility monitoring (Section 3.2)
    a. NDMA was generally removed to at or near the detection limit by the UV/H_2O_2 process at OCWD's AWPF. PDMWD uses a UV/HOCl process which showed similarly low but slightly higher NDMA concentrations in post-UV-AOP water. Previous work by the research team has shown that UV/HOCl may result in lower NDMA removal compared to UV/H_2O_2, potentially due to an increase in formation of NDMA immediately after treatment related to increased chloramines.
    b. NDMA precursors were greater than 98 percent removed by RO in all sampling events (at OCWD and PDMWD), underscoring the efficacy of this treatment process for the removal of NDMA precursors.
    c. The UV/AOP process varied in its efficacy for removal of NDMA precursors. In most cases, precursors were slightly removed. However, in one sampling event, UV/H_2O_2 at OCWD resulted in an increase in the concentration of NDMA precursors.
    d. Certain EEMs components (tryptophan-like compounds) were closely correlated with NDMA precursors at both OCWD and PDMWD, suggesting NDMA precursors may share some common characteristics with these types of compounds.
3. Impact of membrane cleaning on NDMA and NDMA precursor removal (Section 3.3)

    a. Sampling of all OCWD RO membrane units (20 total) showed an average rejection of 97.3 to 99.3 percent for NDMA precursors. NDMA rejection was much lower, as expected.
    b. There was no discernable or significant negative impact of RO membrane cleaning on NDMA precursor rejection, except for a temporary decline in rejection for a few days after cleaning, which is commonly observed for other constituents. Different membrane types may respond differently to the same membrane cleaning process.
    c. Rejection of NDMA declined in the four weeks that were sampled following a membrane cleaning. RO is known to only partially remove NDMA and thus the observed decline in NDMA rejection after membrane cleaning is not as important from the perspective of NDMA compliance, as the subsequent UV-AOP step can be relied upon to remove NDMA.
4. Contribution of NDMA precursors to treated water from treatment plant chemicals (Section 3.4)
    a. The chemical additions to advanced treated water tested here would each be expected to contribute less than 1 ng/L of N-nitrosamines to the finished water. Clarifloc polymer was the exception at 4.3 ng/L of NPIP. However, at the polymer concentration used in the treated water, the addition would be insignificant.
5. Impact of UV-AOP scenarios on NDMA precursors and non-target trace organics (Section 3.5)
    a. NDMA was removed to at or near the detection limit by UV-AOP in all pilot test oxidant scenarios (H_2O_2, HOCl, supplemental chloramine, and residual chloramine). However, NDMA precursor removal was more variable. In the first event (all four oxidant conditions), precursors were removed by UV-AOP to below or near detection limit for all oxidants. In the second event (only H2O2 and HOCl), there was no statistically significant removal.
    b. Based on non-target analysis and the total number of compounds detected/qualified, many compounds were removed by UV-AOP, and some unique transformation products were formed, for all four oxidant scenarios. Compounds with both hydrophilic and hydrophobic character were removed and formed. More compounds were removed by UV/H_2O_2 and UV/HOCl compared to UV/chloramines (both supplemental and residual chloramines).
    c. Non-target analysis was demonstrated to be a powerful tool for assessing the water quality polishing performance of UV-AOP. For example, LC-qTOF/MS revealed that greater than 98 percent of the total compound peak area (which is related to concentration) was removed by UV/H_2O_2 and UV/HOCl while only 61 to 65 percent was removed by UV/chloramine (for supplemental or residual chloramine).

3.7 Recommended Next Steps

This work has clearly demonstrated the variability in water quality and trace organics concentration at advanced water treatment plants, even over the course of a single day, related to the fact that the source water quality can be highly variable. Fortunately, studies have shown that RO is highly effective at removing trace organics. This study demonstrated that RO is an excellent barrier to NDMA precursors. The UV-AOP process was less effective and more variable with respect to removal of NDMA precursors.

In this study, the application of advanced mass spectrometry methods to assess UV-AOP performance showed the occurrence of hundreds to thousands of non-target, organic compounds, as well as the removal of a portion of them, and the formation of some unique compounds. More work is needed to develop and standardize non-target analysis for use to benchmark treatment performance. A more thorough evaluation is needed of the mechanistic processes resulting in the differences seen here for AOPs utilizing different oxidants. Work is also needed to confirm the identity of specific compounds, quantify their occurrence, and assess their risk to human health to ensure that water providers continue to provide safe and reliable water. Some work done by the project team has shown that UV-AOP treated waters are generally less responsive to toxicity-indicating bioassays than conventional drinking waters, but future work should expand the complementary use of bioassays and non-target analysis to further assess the impacts of AOP conditions.

Finally, further optimization of advanced treatment (e.g., UV-AOP conditions/oxidants, choice of RO membrane products, etc.) is needed to maximize the removal of NDMA precursors for those potable reuse utilities concerned with any observed NDMA rebound in finished waters based on local regulatory limits.

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Appendix A – Additional Data Figures

Re: Section 3.1.2.2:

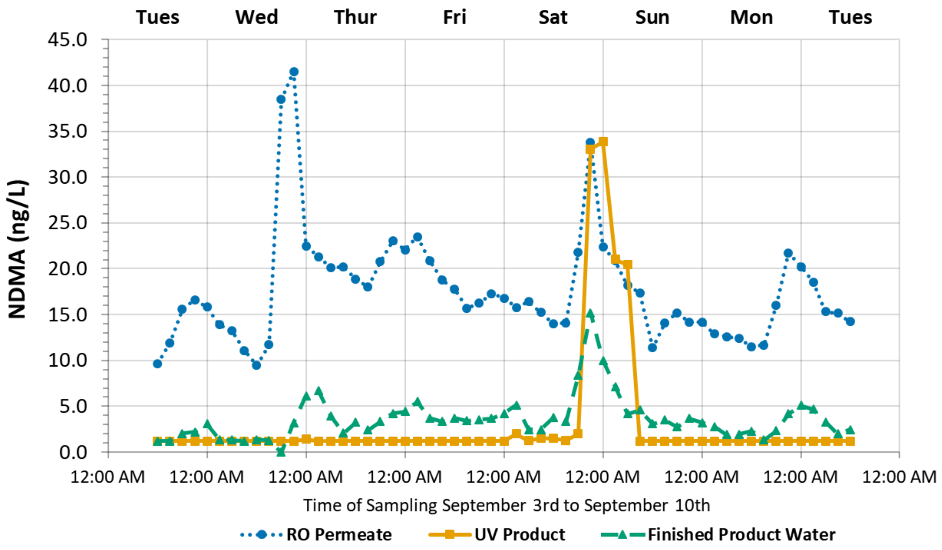

Figure i.—NDMA concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

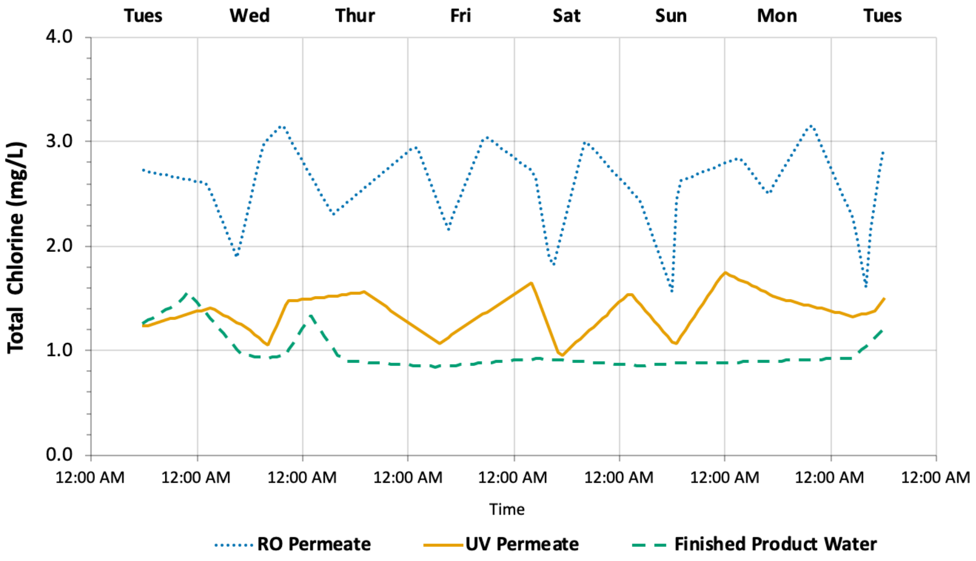

Figure ii.—Total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV-AOP product water, and finished product water over 7 consecutive days measured every 3 hours

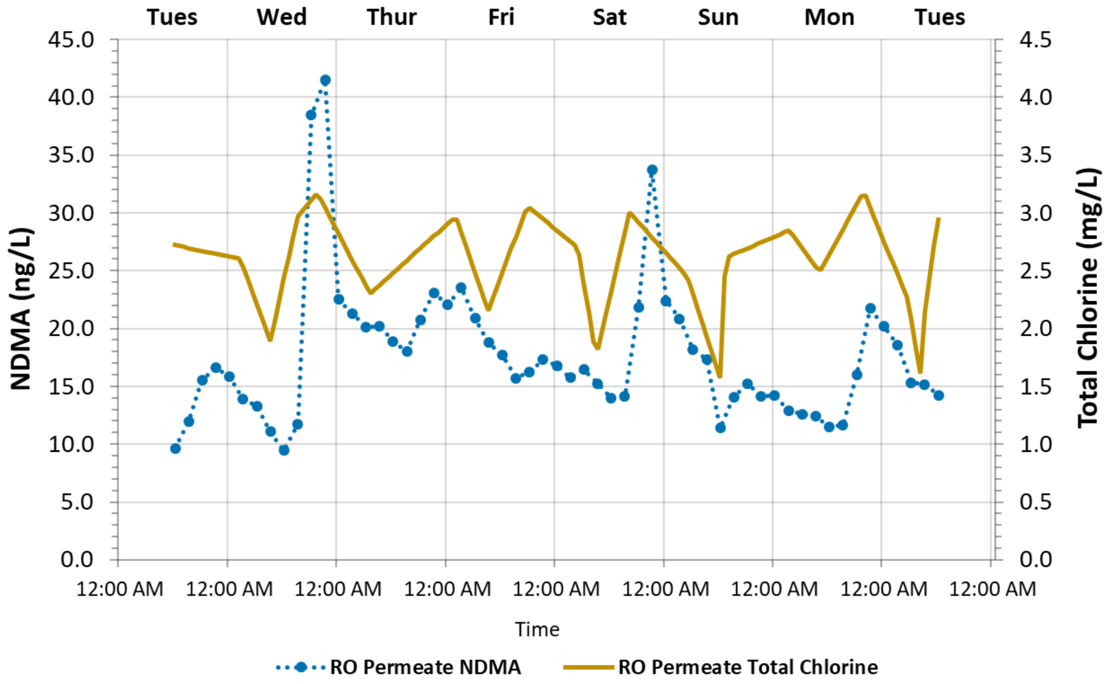

Figure iii.—Total chlorine concentration v. NDMA concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV-AOP product water, and finished product water over 7 consecutive days measured every 3 hours

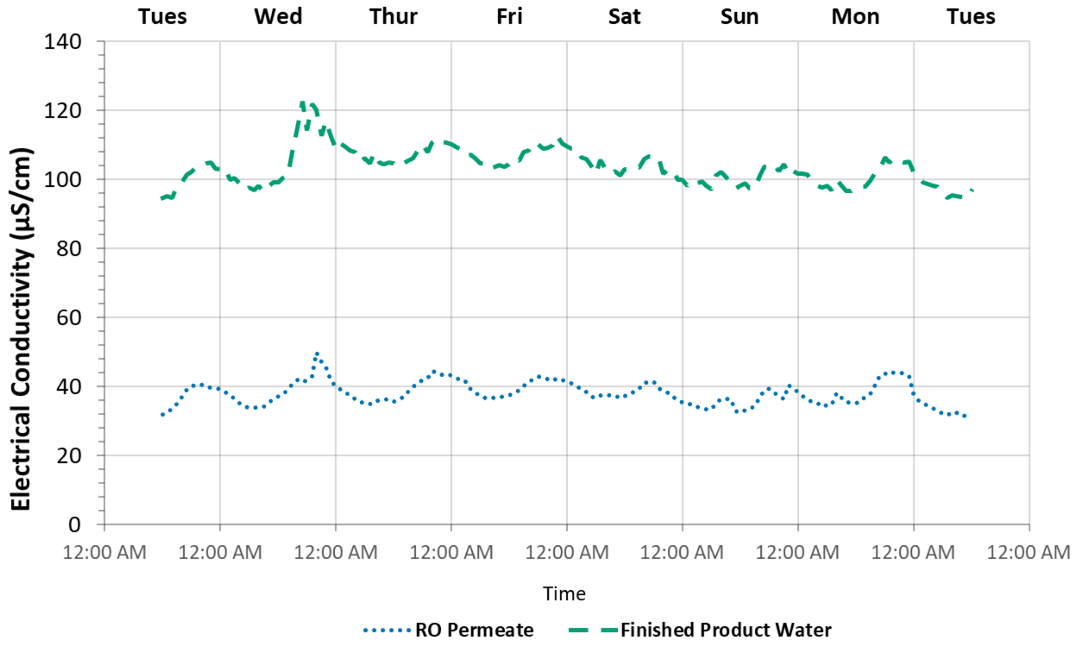

Figure iv.—Electrical conductivity (EC) concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV-AOP product water, and finished product water over 7 consecutive days measured every 3 hours

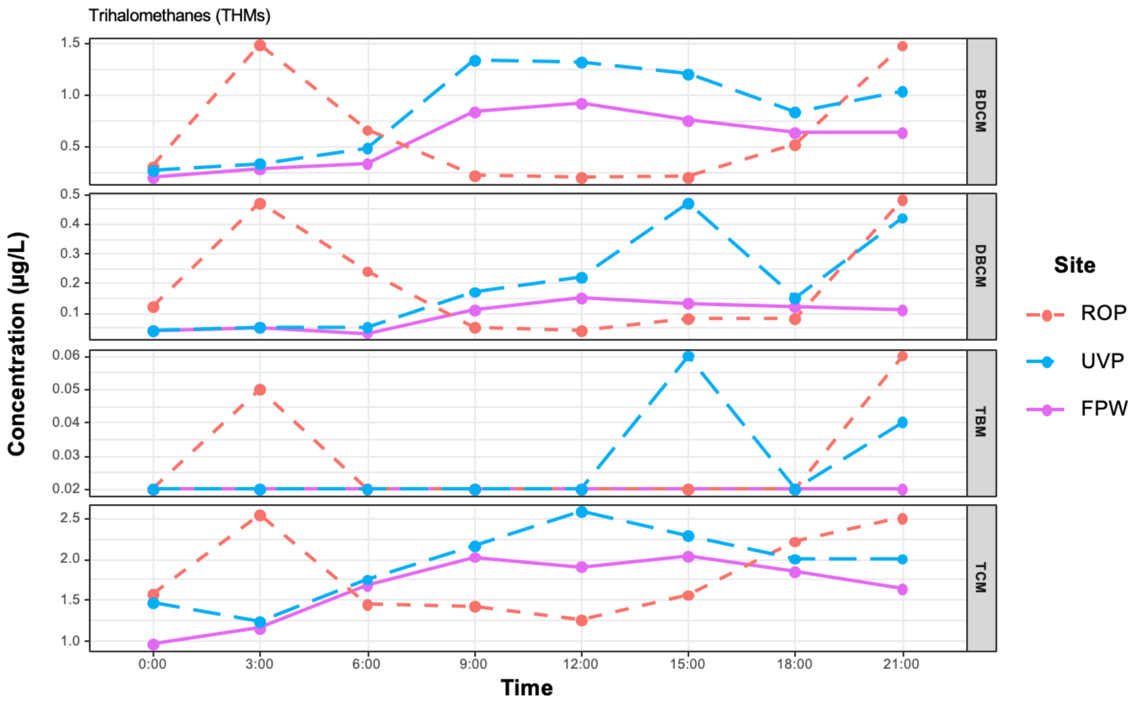

Figure v.—Trihalomethane concentration [bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM), and trichloromethane (TCM)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

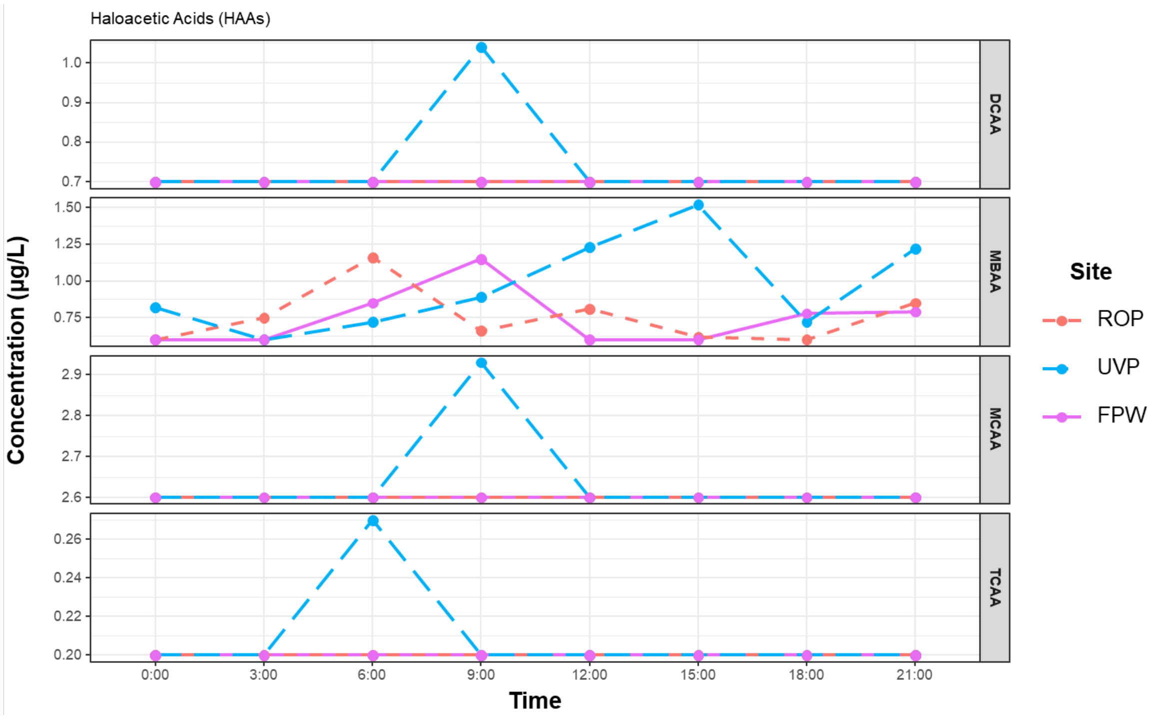

Figure vi.—Haloacetic acid concentration [bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

Re: Section 3.1.2.3:

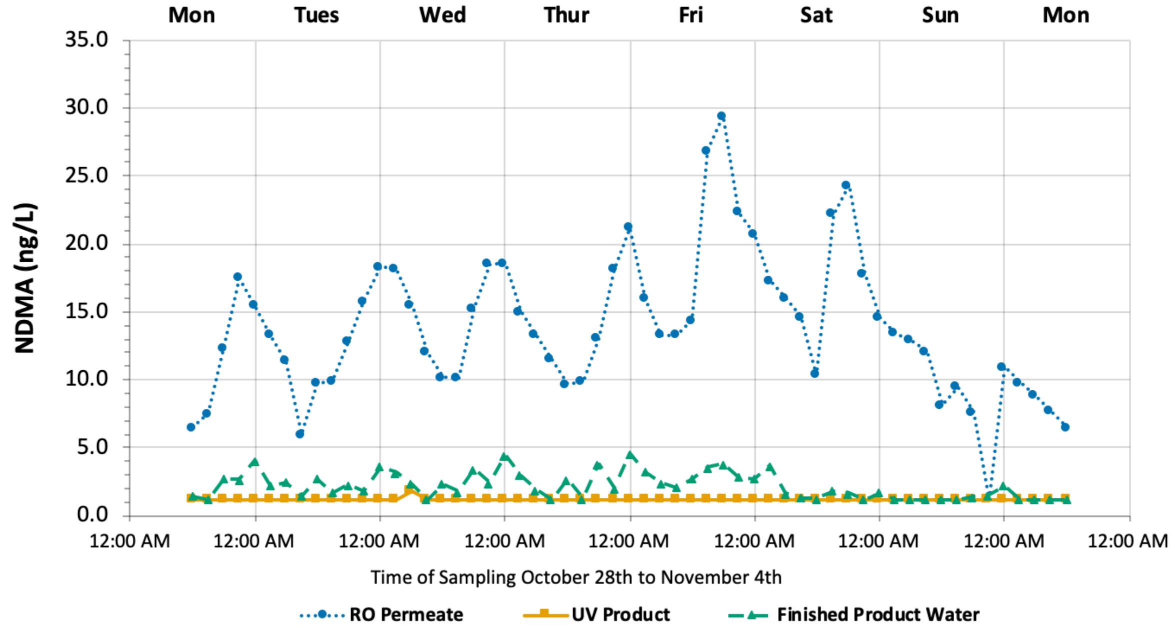

Figure vii.—NDMA concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

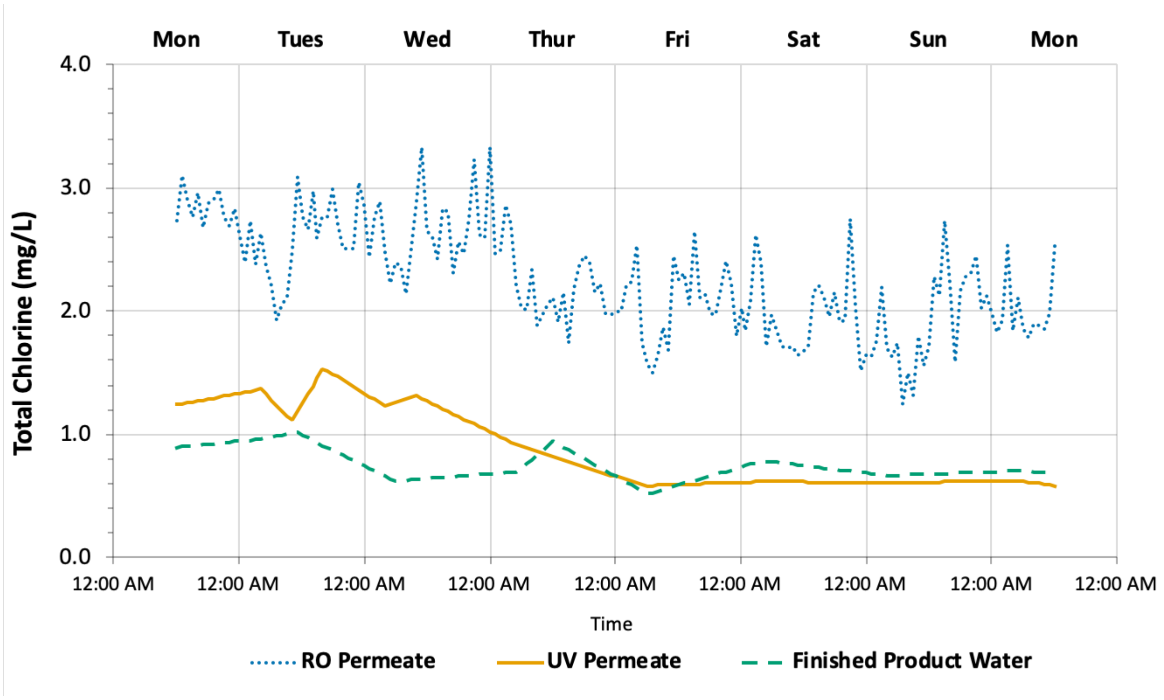

Figure viii.—Total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

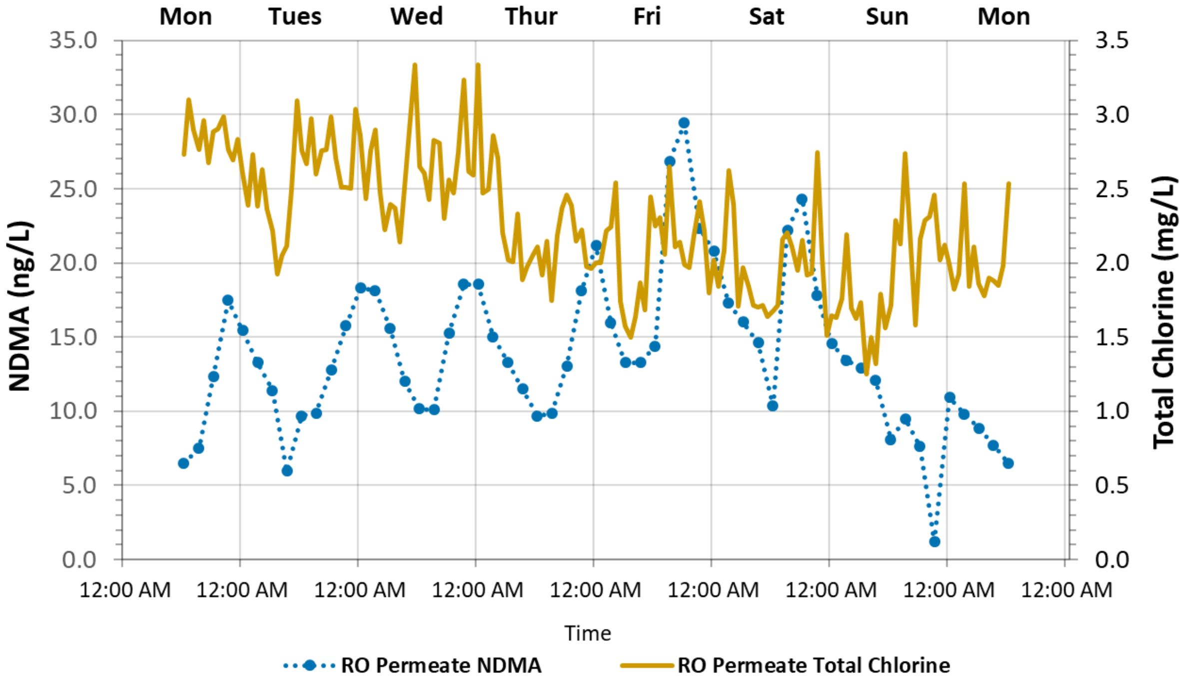

Figure ix.—NDMA concentration versus total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

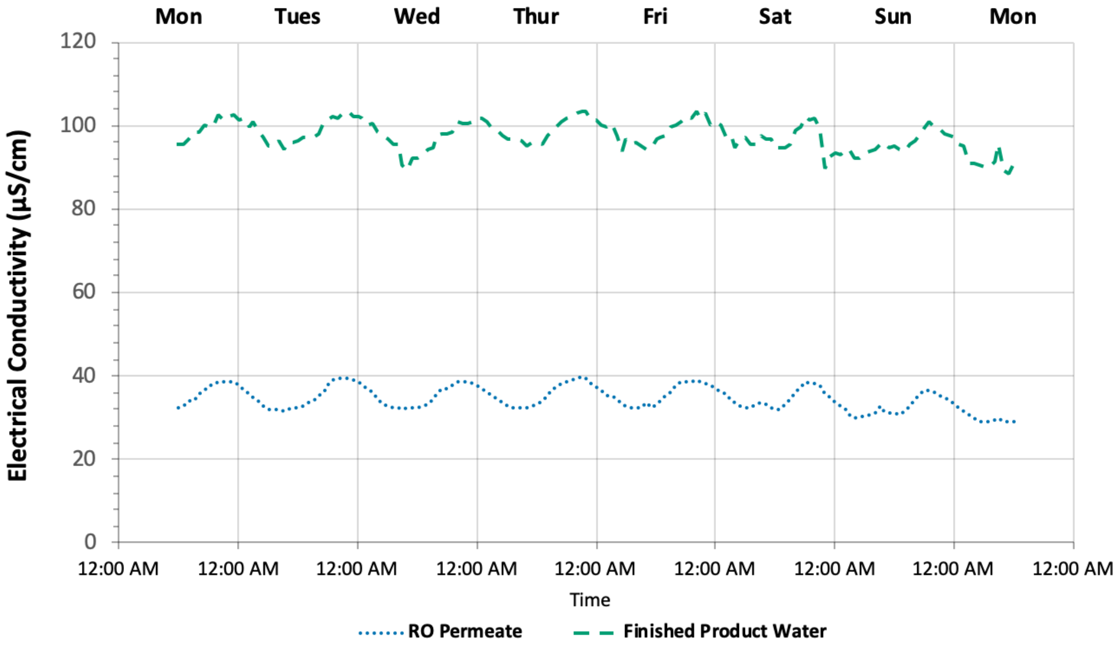

Figure x.—Electrical conductivity in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

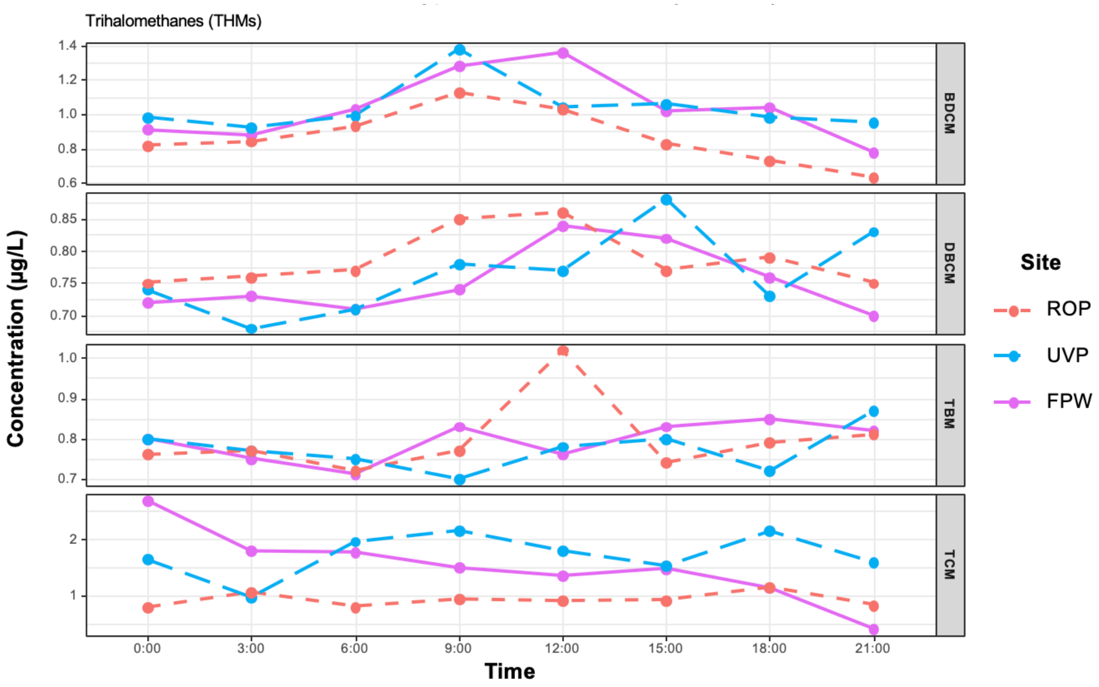

Figure xi.—Trihalomethane concentration [bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM), and trichloromethane (TCM)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

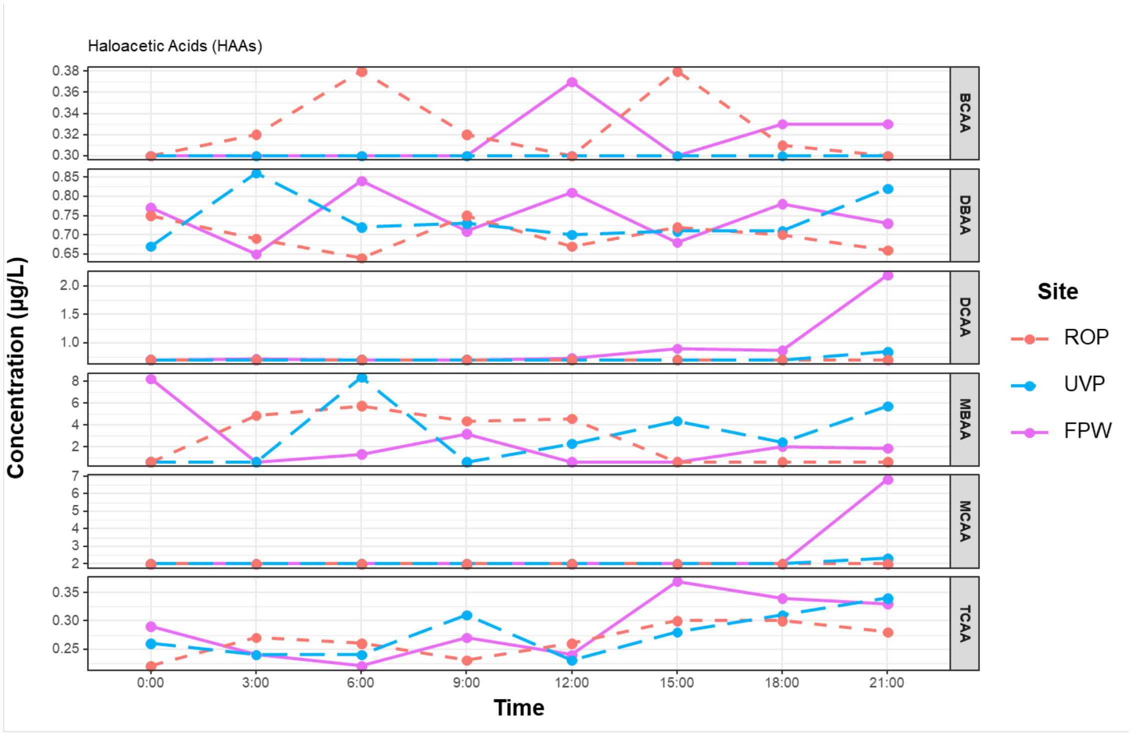

Figure xii.—Haloacetic acid concentration [bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

Re: Section 3.1.2.4:

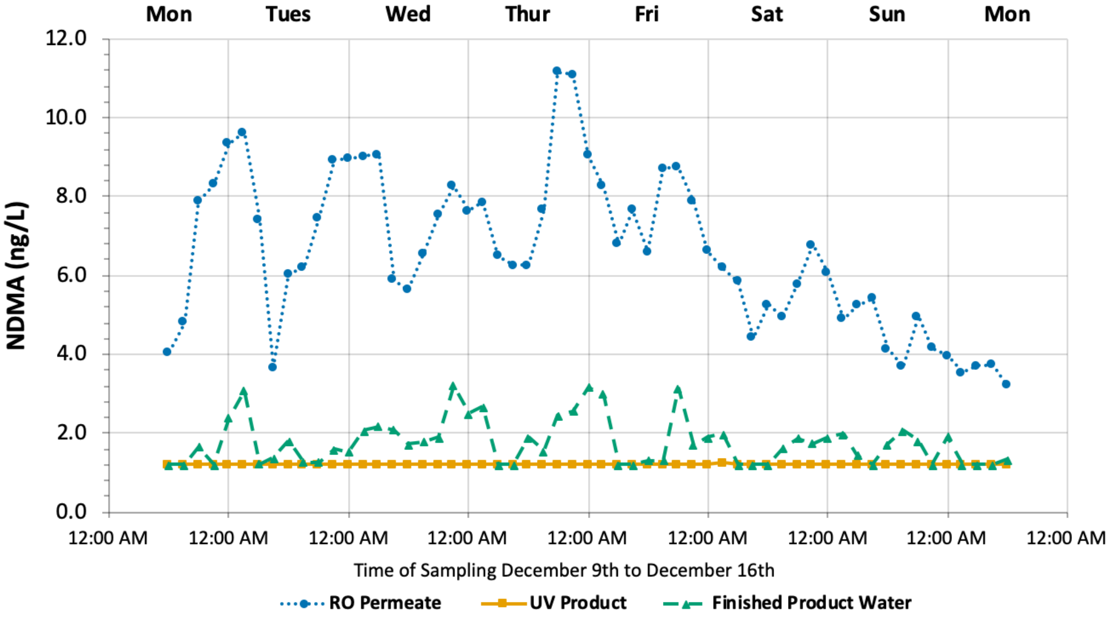

Figure xiii.—NDMA concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

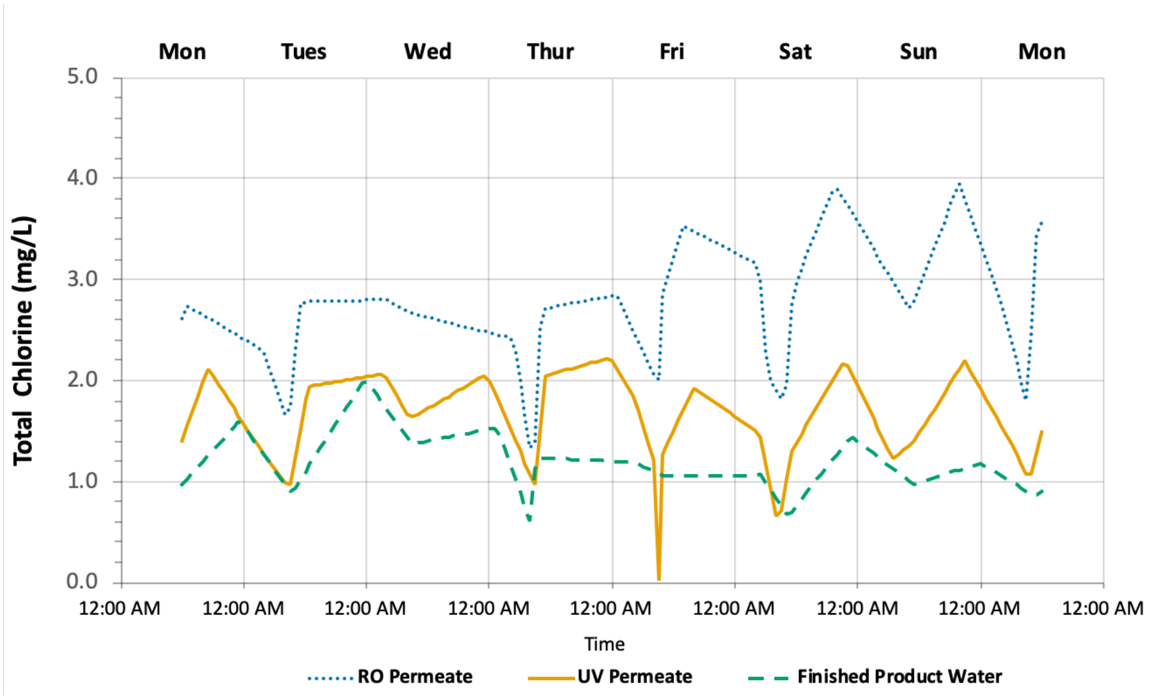

Figure xiv.—Total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

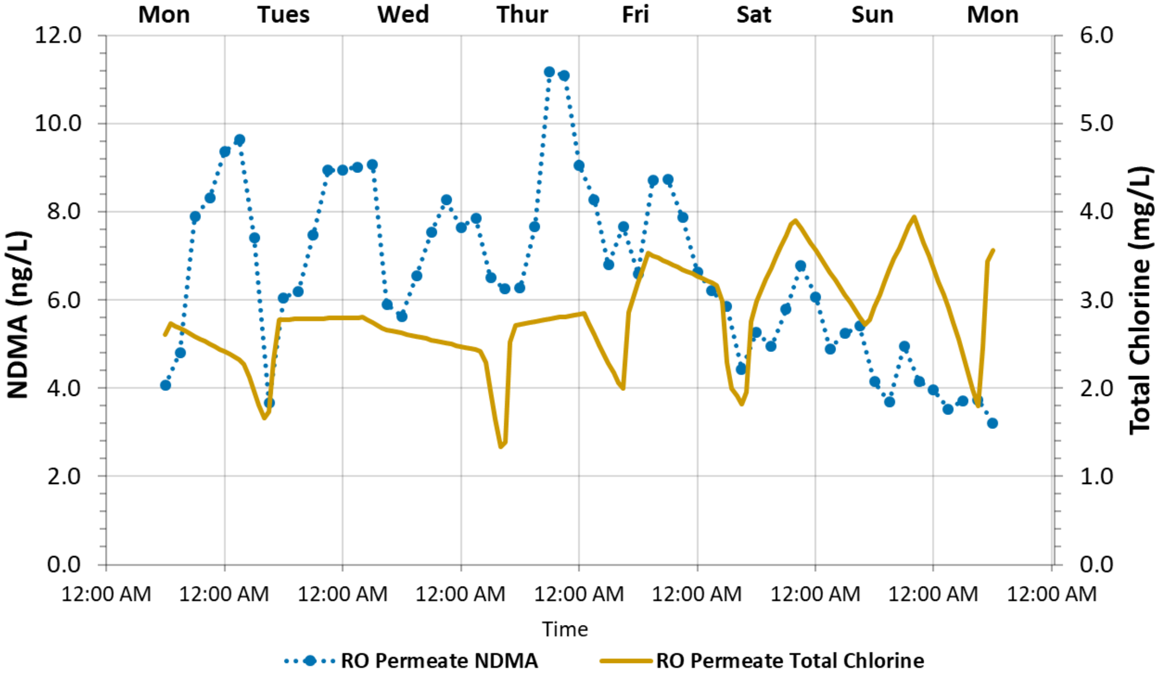

Figure xv.—NDMA concentration versus total chlorine concentration in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

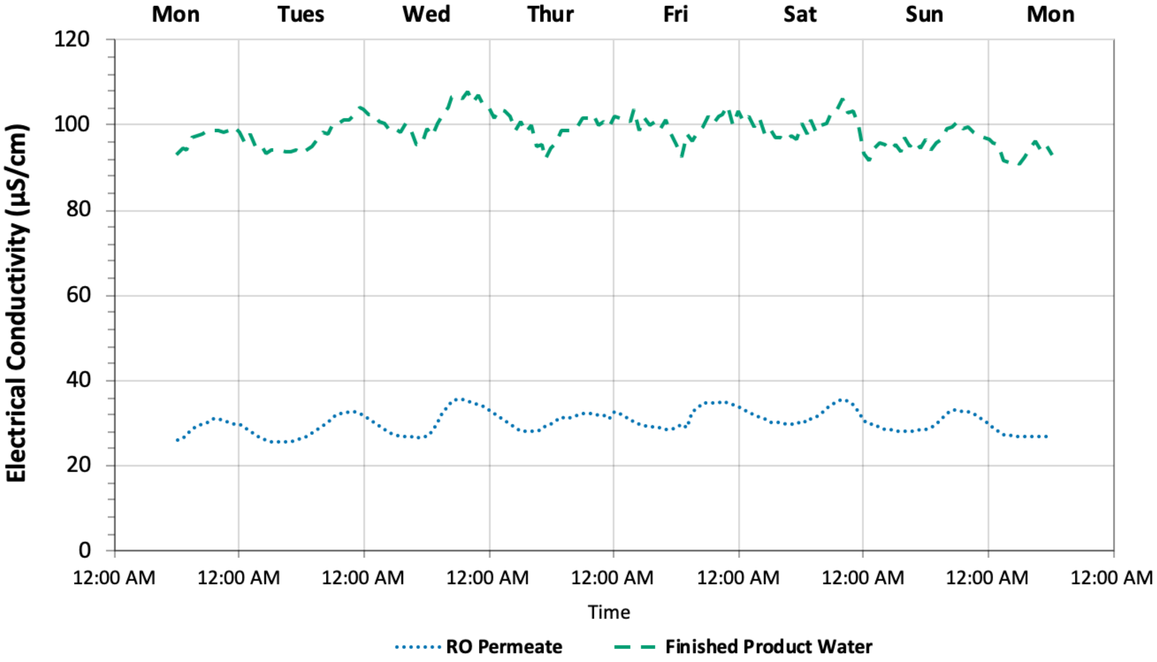

Figure xvi.—Electrical conductivity in the OCWD AWPF reverse osmosis (RO) permeate, UV product water, and finished product water over 7 consecutive days (measured every 3 hours)

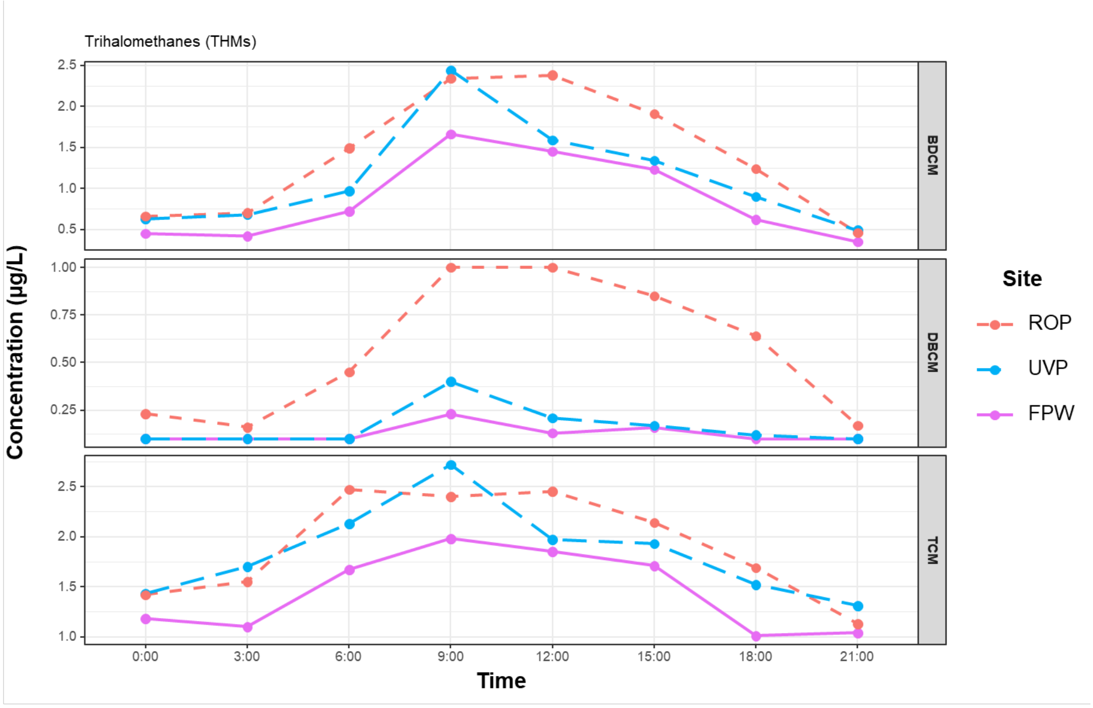

Figure xvii.—Trihalomethane concentration [bromodichloromethane (BDCM), dibromochloromethane (DBCM), bromoform (TBM), and trichloromethane (TCM)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day

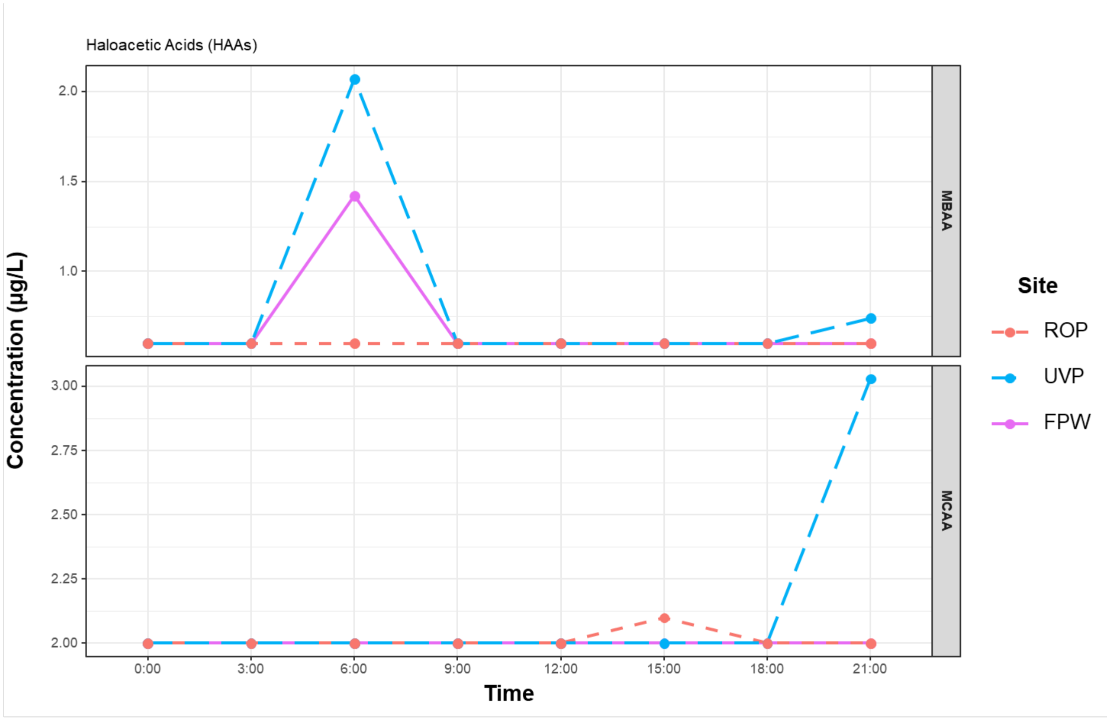

Figure xviii.—Haloacetic acid concentration [bromochloroacetic acid (BCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA)] in Q1, ROF, ROP, UVP, and FPW measured every 3 hours over 1 day