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PROJECT NO.
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Defining Potential Chemical Peaks and Management Options

CALIFORNIA
Water Boards
STATE WATER RESOURCES CONTROL BOARD
REGIONAL WATER QUALITY CONTROL BOARDS

Defining Potential Chemical Peaks and Management Options

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Abstract and Benefits

Abstract:

In response to research recommendations from the California State Water Resources Control Board's Expert Panel on Direct Potable Reuse (DPR), this research addresses the presence and cause of chemical peaks that can escape full advanced treatment (FAT) of recycled water. A literature review, three case studies at full-scale FAT facilities, and the results of experimentation on commercial total organic carbon (TOC) analyzers are presented in this report. It was found that FAT does an excellent job of removing contaminants from recycled water, yet low molecular weight (< 200 Daltons), uncharged volatile organic compounds (VOCs) can escape FAT at full-scale facilities. Chemical monitoring and source control programs at the Orange County Water District Groundwater Replenishment System, the Public Utilities Board of Singapore NEWater Program, and the City of San Diego Pure Water Program provide examples of strategies that should be considered by utilities implementing potable reuse systems without environmental buffers. Online monitoring of TOC with no more frequent than a fifteen minute sampling interval is recommended for DPR projects as a feasible option for capturing chemical peaks. Additional treatment barriers in conjunction with FAT should be considered, for example ozone/biological activated carbon, air stripping, activated carbon, and additional reverse osmosis and/or advanced oxidation. Where possible, "small reservoirs" should be considered given the benefits for chemical peak "averaging" due to blending. Overall, utilities implementing DPR should pursue a balanced approach to control chemical peaks that includes an appropriate combination of two or more of the following: source control, enhanced monitoring, additional treatment barriers, and/or blending.

Benefits:

- This research addresses some of the key concerns identified by the Expert Panel on Direct Potable Reuse.
- The literature review identifies families of compounds that can escape FAT at full-scale facilities.
- Additional treatment processes (including blending) that are appropriate to dampen potential chemical peaks are presented.
- Full-scale FAT facility case studies describe how these utilities address chemical peaks.
- Results are presented from the review and experimentation of commercial on-line TOC analyzers to measure chemical peaks.
- This research, along with the other State of California sponsored DPR research, will help regulators and utilities address the challenges of potable reuse without significant environmental buffers.

Keywords: Direct Potable Reuse, DPR, Chemical Peaks, Full Advanced Treatment, Total Organic Carbon, TOC Analyzer

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Acronyms and Abbreviations

µg/L	Micrograms per Liter
A/W	Air to water ratio
AB	California Assembly Bill
AOP	Advanced oxidation processes
AWTF	Advanced water treatment facility
AWPF	Advanced water purification facility
BAC	Biological activated carbon
CAS	Chemical abstract service
CCP	Critical Control Point
CEC	Constituents of emerging concern
CSTR	Continuously stirred tank reactor
CWA	Clean water act
CWRP	Changi Water Reclamation Plant
DAF	Dissolved air floatation
DBP	Disinfection byproducts
DDW	California Division of Drinking Water
DEET	*N,N'*-diethyl-*m*-toluamide
DMAc	N,N-dimethylacetamide
DPR	Direct potable reuse
DWTP	Drinking water treatment plant
EDC	Endocrine disrupting compound
EPA	United States Environmental Protection Agency
FAT	Full advanced treatment
g/mol	Grams per mole
GAC	Granular activated carbon
GC-MS	Gas Chromatography-Mass Spectrometry
GWRS	Groundwater Replenishment System
HAA	Haloacetic acid
HAN	Haloacetonitriles
Hcp	Henry's law solubility constant
HRT	Hydraulic retention time
HTC	High temperature combustion
H_{yc}	Henry's law constant
IC	Inorganic carbon
ICR	Inorganic carbon removal
IPR	Indirect potable reuse
IQR	Interquartile range
JWRP	Jurong Water Reclamation Plant
KNF	Kranji NEWater facility
KWRP	Kranji Water Reclamation Plant

lb	Pound
LMW	Low molecular weight
MBR	Membrane bioreactor
MCL	Maximum
MF	Microfiltration
mg/L	Milligram per Liter
MGD	Million gallons per day
MIBK	Methyl isobutyl ketone
MITC	Methylisothiocyanate
NCWRP	North City Water Reclamation Plant
NdN	Biological nitrification/denitrification
NDEA	N-Nitrosodiethylamine
NDIR	Non-dispersive infrared
NDMA	N-Nitrosodimethylamine
ng/L	Nanogram per Liter
NL	Notification limit
NMOR	N-nitrosomorpholine
NPDES	National pollutant discharge elimination system
NPOC	Non-purgeable organic carbon
NRC	National Resource Council
NSAID	Nonsteroidal anti-inflammatory drug
OC San	Orange County Sanitation District
OCWD	Orange County Water District
OOP	Operational Optimization Plan
PAC	Powdered activated carbon
PWDF	Pure Water Demonstration Facility
PFAS	Per- and polyfluorinated alkyl substances
PID	Photo-ionization detector
PLWTP	Point Loma Wastewater Treatment Plant
POC	Purgeable organic carbon
POTW	Publicly owned treatment work
ppb	Parts per billion
PPCP	Pharmaceuticals and personal care products
PTA	Packed tower aeration
PUB	Singapore Public Utilities Board
PUO	Persulfate-ultraviolet oxidation
Q1	Quartile 1
Q3	Quartile 3
RO	Reverse osmosis
ROF	Reverse osmosis feed
ROP	Reverse osmosis permeate
RWA	Raw water augmentation

RWQCB	California Regional Water Quality Control Board
SB	California Senate Bill
SBWRP	South Bay Water Reclamation Plant
SST	System suitability testing
SWA	Surface water augmentation
SWRCB	State Water Resources Control Board
TC	Total carbon
TCE	Trichloroethylene
TCEP	tris(2-carboxyethyl)phosphine
TCP	Trichloropropane
TDWA	Treated drinking water augmentation
THM	Trihalomethane
TOC	Total organic carbon
TSAO	Two stage advanced oxidation
TWG	Technical working group
UF	Ultrafiltration
UV	Ultraviolet Disinfection
UPWRP	Ulu Pandan Water Reclamation Plant
UVT	Ultraviolet transmittance
VOC	Volatile organic compounds
WRF	Water Research Foundation
WRP	Water reclamation plant
WWTP	Wastewater treatment plant

Executive Summary

This project is the fourth of the five research projects managed by The Water Research Foundation (WRF) to support the California State Water Resources Control Board (SWRCB) in developing criteria and guidelines for direct potable reuse (DPR).

The objectives of this research were to:

1. Evaluate the potential for certain chemicals to persist through advanced water treatment systems and options for the detection of chemical peaks;
2. Evaluate the potential for "averaging" (reduction) of such chemical peaks through treatment and/or blending;
3. Review case studies of source control programs of existing indirect potable reuse (IPR) facilities and make related recommendations for future DPR programs; and,
4. Collect data with respect to the ability of commercially available online total organic carbon (TOC) analyzers to accurately measure chemicals that may persist through advanced water treatment.

ES.1 Chemical Removal by Full Advanced Treatment

The report reviews and summarizes chemical removal that is accomplished by full advanced treatment (FAT). The FAT process train in California is defined by regulation as including reverse osmosis (RO) and an advanced oxidation process (AOP). Membrane filtration (i.e., microfiltration or ultrafiltration) typically precedes the RO process to provide suitable feedwater and plays a critical role in achieving pathogen removal requirements, but plays a negligible role in chemical removal.

The multibarrier approach associated with FAT has been adopted to protect public health in potable reuse applications throughout the world. The purpose of this evaluation was to identify known chemicals that could potentially challenge the FAT treatment train.

With respect to RO, numerous studies have investigated rejection of organic compounds by RO membranes. Due to rejection typically occurring via electrostatic repulsion and/or Donnan exclusion, adsorption, or size exclusion, the most likely compounds to have low rejection by RO membranes must meet each of following criteria: (1) uncharged, (2) hydrophilic and/or polar, and (3) low molecular weight (LMW). This general trend is reported extensively throughout the literature.

For this evaluation, data from several studies on RO rejection of organic compounds were reviewed and compiled to identify chemicals and chemical families that have lesser rejection by RO (see Table ES-1). Volatile organic compounds (VOCs) are among the chemical families most prone to have low rejection, as the functional chemistry that makes them volatile (low molecular weight, uncharged, etc.) allows for passage through the membrane. These compounds include haloalkanes, haloalkenes, halobenzenes, alkylbenzenes, and LMW oxygenated compounds.

Table ES-1. Summary of RO Rejection of Organic Compounds and Chemical Families.

Chemical Family	Sub-group	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
VOCs	Solvents and Industrial Compounds	Ethers	Halobenzenes; 1,1,2-Trichloroethylene	Nitriles; Haloalkenes Benzotriazole
	Haloalkanes	CCl_4; Ethanes with 3-4 Cl atoms; Most C_4+ haloalkanes	Some C_1-C_3 haloalkanes	C_1-C_2 haloalkanes with 1-2 halogen atoms
	Alkylbenzenes	C_{10+}	C_6-C_9	
	Pesticides/ Herbicides	1,2,3-Trichloropropane		Methylisothiocyanate (MITC)
LMW Oxygenated Compounds	Alcohols	Branched C_{4+} alcohols	Isopropyl alcohol; Most unbranched alcohols	Methanol; Ethanol
	Aldehydes, Ketones	Methyl isobutyl ketone (MIBK)	Acetone; Unbranched C_3-C_6 Ketones	Formaldehyde; C_1-C_6 Aldehydes
PPCPs	Flame Retardants	Chlorophosphates; PFAS		
	Pharmaceuticals	Steroids; β-blockers; NSAIDs; X-ray Contrast Media		
DBPs	Nitrosamines	C_{4+} nitrosamines; NMOR	NDMA; NDEA	
	Halogenated DBPs	Haloacetic Acids (HAAs)	Haloacetonitriles (HANs)	Trihalomethanes (THMs)

References: Howe et al. 2019, Zeng et al. 2016, Rodriguez et al. 2012, Snyder et al. 2007a, Kiso et al. 2011, Tackaert et al. 2019, Fujioka et al. 2012; Doederer et al. 2014; Alotaibi et al. 2015

Also a part of FAT following RO, AOPs are processes that utilize hydroxyl radicals to oxidize organic and inorganic contaminants that may be present in the RO permeate. AOPs are most effective at removing organic compounds containing electron-rich moieties such as aromatic structures. PPCPs (pharmaceuticals and personal care products) and pesticides exhibit greater than 90% rejection by RO membranes and greater than 90% removal by AOP, thus the FAT process train provides robust protection from these compounds.

VOCs have poorer rejection by RO than PPCPs, but these compounds are less studied in AOP systems. To evaluate their potential removal, reaction rate constants between target compounds and hydroxyl radicals were compared to the rate constant between hydroxyl radicals and 1,4-dioxane. Challenge testing of AOP processes is often performed by measuring the degradation of 1,4-dioxane, with a regulatory requirement in California of a minimum 0.5 log (69%) removal. Compounds identified to potentially persist through RO treatment were therefore classified as having good removal during AOP (>1,4-dioxane) or poor removal during AOP (<1,4-dioxane), as shown in Table ES-2.

Table ES-2. Predicted Removal of Organic Compounds via AOP.

Family	Greater than 1,4-dioxane	Less than 1,4-dioxane
VOCs	Haloalkenes Halobenzenes Alkylbenzenes C_4+ Alcohols C_4+ Aldehydes C_6+ Ketones Acrylonitrile Benzotriazole	C_1-C_3 Haloalkanes C_1-C_3 Alcohols C_1-C_3 Aldehydes C_3-C_5 Ketones Acetonitrile MITC
PPCPs	Most pharmaceuticals	Flame Retardants
DBPs	Nitrosamines[1]	THMs

Notes: [1] High removal in UV/AOP systems

References: Drewes et al. 2008, Howe et al. 2019, Ahmed et al. 2017, Drewes et al. 2006, Buxton et al. 1988, Swancutt et al. 2010; Bahnmüller et al. 2015

ES.1.1 Chemical Families Identified as Having Potential for Incomplete Removal by FAT

Based on the above-described literature review and analysis, a short list of chemical families was identified as having intermediate to poor rejection by RO membranes and poor removal by AOP (less efficient than 1,4-dioxane):

1. Low molecular weight (LMW) haloalkanes
2. LMW alcohols, aldehydes, and ketones
3. Acetonitrile
4. Methylisothiocyanate (MITC)
5. Trihalomethanes (THMs)

Industrial use of solvents including LMW haloalkanes, alcohols, aldehydes, ketones, and acetonitrile make these the compounds with the highest potential to comprise a chemical peak persisting through FAT. LMW alcohols, aldehydes, and ketones can also be biologically produced within the wastewater treatment plant (WWTP). For example, a 2018 reported spill of isopropyl alcohol into the Orange County Sanitation District (OC San) collection system was the likely cause of a corresponding spike of acetone seen at the Orange County Water District (OCWD) Groundwater Replenishment System (GWRS) RO facility, discussed in this report. Similarly, MITC is a breakdown product of an herbicide used for control of vegetation in sewer systems and could potentially persist through FAT. Trihalomethanes have much lower production volumes, with chloroform being the most likely to be discharged into the collection system.

ES.2 Additional Barriers to Accomplish Peak "Averaging"

The established FAT treatment train provides a robust multi-barrier approach for the removal of pathogens and chemical contaminants from water. However, low molecular weight (LMW) chemicals have been documented to pass through FAT facilities during rare events (i.e., illicit discharges) and known chemical families have been identified, discussed above, which could pass through FAT if present in high enough concentrations.

For this project, additional barriers were reviewed, listed below, that are able to provide some reduction or averaging of chemical peaks. However, to provide reliability and resilience in a DPR program, a balance of source control, monitoring, treatment, and blending is required.

1. Ozone/Biological Activated Carbon (BAC) as a Pretreatment – Ozonation oxidizes aromatic rings and complex bonds in organic molecules and generates hydroxyl radicals, which combined eliminates many constituents of emerging concern to below levels of detection. These oxidized organics result in LMW organic compounds such as LMW aldehydes and ketones that can more easily pass through RO. However, in combination with a biological process, such as biological activated carbon (BAC), the ozone/BAC process develops a biological community that is capable of effectively removing these LMW organics that result as a byproduct from the oxidation process. The BAC is continuously exposed to these LMW compounds produced as an oxidation byproduct and effectively removes them (e.g., acetone, formaldehyde) along with other compounds of concern, such as NDMA.
2. Air Stripping – Air stripping is a treatment technology utilized to remove volatile compounds from water. For this evaluation, compounds with the potential to persist through FAT were classified as having potentially efficient removal via air stripping (e.g., via packed tower aeration, PTA) if their respective Henry's Law constants were greater than 0.01 (dimensionless); these include alkylbenzenes, halobenzenes, haloalkanes, haloalkenes, methylene chloride, and THMs. LMW alcohols, aldehydes, ketones, and acetonitrile are not efficiently removed by air stripping. Due to the unknown nature of a potential chemical peak, an air stripping system could be designed to remove compounds with a Henry's Law constant above a baseline value, such as 0.01 as described above.
3. Activated Carbon – Granular activated carbon (GAC) and powdered activated carbon (PAC) remove organic constituents primarily through adsorptive processes. GAC/PAC can remove compounds from non-polar to intermediate polarity, but highly polar volatile compounds have reduced GAC removal efficiencies. LMW alcohols, aldehydes, ketones, and acetonitrile are not efficiently removed by GAC/PAC. The unknown nature of a potential chemical peak requires design criteria of the GAC system to be conservatively set, possibly resulting in over-sized vessels.
4. Additional RO and/or AOP Treatment – While the use of additional RO or additional AOP processes does not increase the robustness (i.e., diversity) of a treatment system, increased removal of chemicals can be achieved via a second pass or recirculation. The second pass RO treatment occurs by passing the RO permeate through an additional RO treatment train, while recirculation sends product water back through the same equipment again during peak events. While compounds with poor to intermediate RO rejection will have similar rejection through the second pass, the total rejection will increase and good removal (>90%) of some compounds, such as some haloalkanes, C4+ ketones, and propanols, could be achieved. Similar to RO, while comparable removal to the initial AOP would occur in a second pass or recirculation AOP process, the additive removal would provide some benefit.
5. Blending – The use of blending for the averaging of chemical peaks has the distinct advantage that it is non-selective, i.e., it has the potential to reduce concentrations of all chemicals equally. To achieve blending of chemical peaks, an additional water source is required. The blending water source can be DPR water that passes through the advanced water treatment facility (AWTF) before and/or after the chemical peak, a raw water during Raw Water Augmentation (RWA) or a finished drinking water during Treated Drinking Water Augmentation (TDWA). Blending can occur in an engineered storage tank, in an impoundment, or within transmission piping.

ES.3 Defining a Chemical Peak

The challenge of differentiating occurrence of true chemical peaks, defined in the scope of this project as due to intentional or unintentional illicit discharges into the sewershed, is to distinguish these disturbances from the normal variations seen in a facility. The measurement (i.e., online TOC) must deviate from the variable baseline (peak height) and be present for a significant length of time (peak width). The use of online TOC analyzers has been widely accepted as the preferred method of RO performance monitoring to ensure membrane and process integrity. For the purposes of this analysis, TOC analyzers are assumed to sufficiently measure the occurrence of the broad spectrum of organic compounds previously discussed.

In order to be classified as a chemical peak due to an illicit discharge, the following criteria must be met:

1. Peak height must exceed a threshold above the normal baseline variation in RO permeate TOC. For the purposes of this discussion, the “baseline threshold” is defined as the TOC threshold above which may indicate a deviation from baseline conditions and could signify the presence of a chemical peak. This baseline threshold can be set as the 75th percentile of annual data (quartile 3) plus 1.5 times the Inter-Quartile Range, IQR, (quartile 3 minus quartile 1). The deviation from normal conditions (exceedance event) does not immediately imply the presence of a chemical peak, but rather requires further investigation before classification as a chemical peak (i.e., consideration of peak width and rate of increase, described below).
2. Peaks must exceed the baseline threshold for at least three consecutive measurements with the online TOC analyzer to qualify as an excursion. To avoid use of errant signals, multiple consecutive data points, with a minimum of three, above the baseline threshold are defined as an “excursion” when attempting to identify the start of a potential peak. An excursion above baseline does not automatically indicate the occurrence of a true chemical peak (as peak width and rate of increase must be considered, described next below).
3. Peaks must last from several hours to days. The combination of dispersion through the sewershed and the WWTP will result in a minimum peak length from several hours to several days long, even if the illicit discharge itself was short-lived or “instantaneous.” The definition of peak width on the scale of hours to days is important to reduce the number of “false positives” that could result in unnecessary operational responses.

It should be noted that although TOC online monitoring is generally done on both the RO feed and RO permeate streams (as related to evaluation of RO integrity and pathogen reduction credits), chemical peak detection in potable reuse facilities is expected to focus on the RO permeate. This is because TOC measurements from the RO feed cannot reliably be used to classify the presence of a chemical peak, since the chemical peak may be a small portion of the TOC in the RO feed and thus be indiscernible, as illustrated from OCWD data review in this study.

Given that chemical peaks are expected to last on the order of hours to days, a fifteen minute minimum sampling interval for the online TOC analyzer is sufficient to detect a chemical peak without the risk of the peak passing through the treatment system undetected. Under the Surface Water Treatment Rule, the minimum required sampling interval for an analysis to be considered continuous is fifteen minutes. It is worth noting that in the six years of data collected, the TOC concentrations were below the baseline threshold >99.5% of the time. Therefore, regular grab sample monitoring of the RO permeate is an ineffective method to identify chemical peaks.

To vet the recommended definition of a chemical peak, real data from the OCWD GWRS RO facility was analyzed using one year of online TOC data for RO permeate from 2018. The baseline threshold was calculated as 0.080 mg/L TOC. Figure ES-1 shows the occurrence of five potential chemical peaks, identified as exceedance events above the baseline threshold, in the month of October that were investigated using the above recommended criteria for qualifying as a chemical peak (i.e., a potential illicit discharge into the sewershed). Of the five exceedance events above the baseline threshold, only Event 2 is likely indicative of a chemical peak due to an illicit discharge. The remaining events did not meet the definition of a chemical peak. The brief exceedances in Event 3 and Event 4 are likely analytical errors, the excursion in Event 1 is indicative of normal variation at the upper end of the baseline condition, and Event 5 (and the second exceedance in Event 3) were suspected to be due to operational events, which was confirmed upon review of OCWD operations records. These short-term spikes, commonly seen in the startup of RO trains, represent an increase in background TOC with similar composition as during normal operation, and do not signify any significant change in permeate water quality that requires additional treatment or mitigation steps.

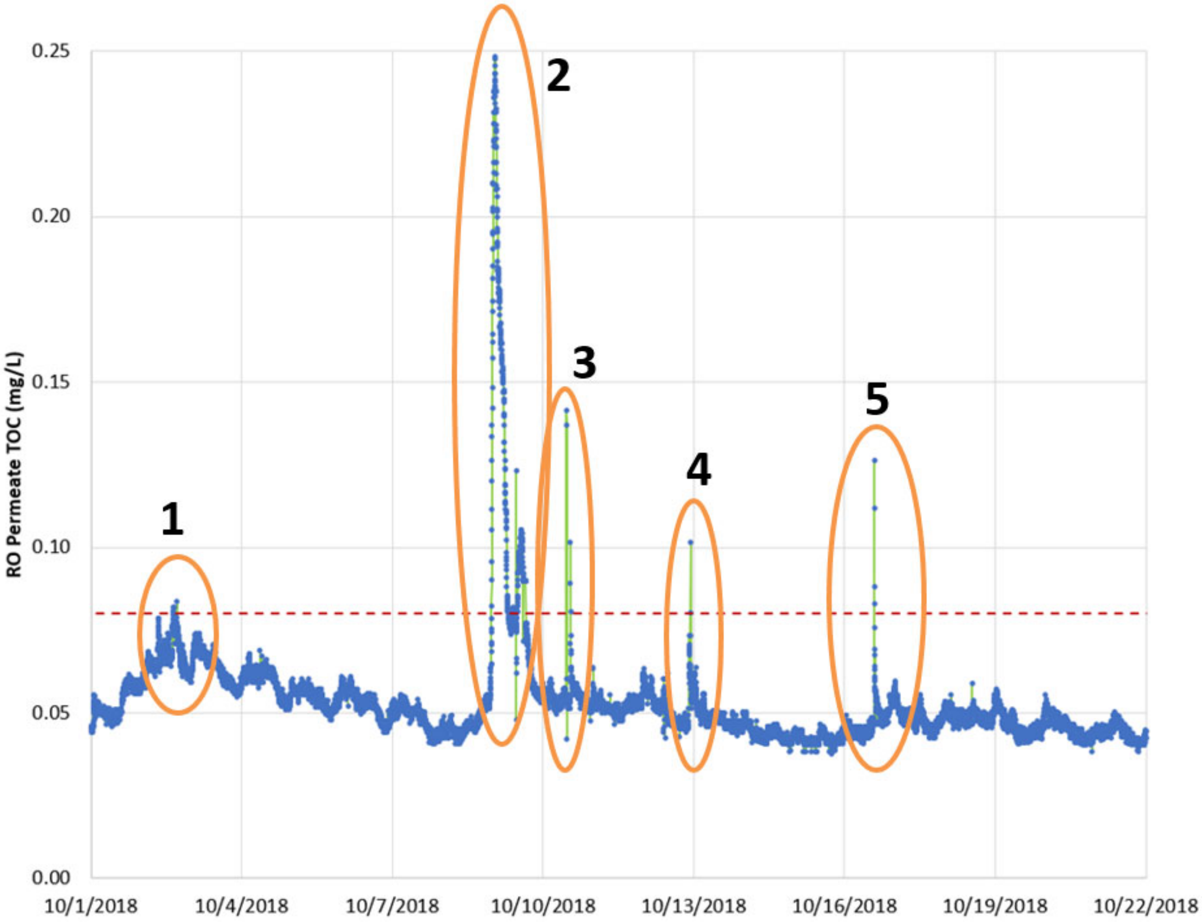

Figure ES-1. Potential Chemical Peaks in RO Permeate at OCWD GWRS (Analyzer: TOC2).
Red dashed line indicates baseline threshold.

ES.4 Source Control Programs of Case Study Utilities

Municipal wastewater contains discharges from residential, commercial, and industrial sources as well as stormwater infiltration/inflow. Source control programs are implemented with the goal of reducing (or eliminating) the discharge of constituents that are difficult to manage from a treatment and environmental standpoint. Industrial flow is commonly commingled with the municipal flow received at wastewater treatment facilities. The United States has a federal National Pretreatment Program that was created as part of the 1972 Clean Water Act. Although it provides a strong foundation in terms of protecting a publicly owned treatment works (POTWs) from industrial user discharges, the program was not originally envisioned to support and protect potable reuse projects.

For potable reuse, it is important to recognize the shift of historically separating sewershed from watershed to a paradigm where the sewershed is seen as a resource to augment potable water supplies. As such, a source control program is critical in creating a safe water supply. To complement or enhance a conventional source control program for potable reuse, online monitoring of the sewershed may be considered to provide early warning to the FAT facility and also help identify the location of the chemical discharges that may impact the source quality.

This report provides a non-exhaustive description of three case study utility source control programs: Orange County Sanitation District (OC San), City of San Diego, and the Public Utilities Board (PUB) of Singapore.

1. OC San – The Groundwater Replenishment System (GWRS) is a joint project of OCWD and OC San featuring an advanced water purification system for potable reuse. OC San maintains a pretreatment program with several innovative features. OC San's service area is comprised of approximately 87% raw wastewater from residential sources and 13% from commercial and industrial sources.
2. City of San Diego – The City of San Diego's source control program is administered by the City's Industrial Wastewater Control Program to apply and enforce federal pretreatment regulations. The North City Water Reclamation Plant will serve effluent to the future North City Pure Water Facility and will have an industrial flow contribution of 2% after the facilities' sewershed is expanded to 52 MGD.
3. Singapore PUB – PUB's source control program was developed to manage wastewater discharge quality to support water reclamation. The source control program consists of multiple components that include regulation of industries discharging to the network and an extensive sewershed monitoring program. The program includes stakeholder engagement among industry, a robust enforcement regime to deter and penalize offenders, monitoring measures, and staff training. Some NEWater facilities in Singapore isolate the industrial flows and do not utilize them for potable reuse applications.

ES.5 Development of an Enhanced Source Control Program for Direct Potable Reuse

Specific to DPR, it is important to understand the impact of chemicals that could adversely impact drinking water quality and the potential sources of such compounds that may enter the sewershed, particularly from industrial dischargers. Measures that can be incorporated into enhanced source control programs for DPR include:

1. Ensuring the appropriate regulatory/legal authority of the source control program;
2. Monitoring/assessment of discharges to the collection system;
3. Source investigation based on a comprehensive inventory of industries/businesses that use/generate chemicals of concern;
4. Maintenance of chemical inventory representing use in the service area;
5. Public outreach programs to encourage dischargers to be partners in protecting the sewershed;
6. Collaboration between the WWTP and AWTF to ensure a response plan for water quality deviations; and,
7. Consideration of real time monitoring of sewershed water quality to proactively mitigate effects of chemicals peaks.

Real time monitoring of sewershed water quality may be particularly useful in areas with high presence of industrial dischargers, where chemical peaks are expected to be more prevalent. This report describes the following monitored parameters that have shown to be effective at detecting chemical peaks in the sewershed:

1. General water quality parameters (e.g., conductivity, pH, temperature, and oxidation reduction potential) to identify water quality excursions that can co-occur during illicit discharges.
2. Volatile organic chemicals (such as via photo-ionization detector or microbial electrochemical sensor).

Overall, though a DPR-tailored source control program will diminish unwanted chemical discharges, expectations must be realistic regarding the effectiveness of such programs. Source control programs are not assumed to eliminate chemical peaks entirely, though they are important to reduce such occurrences.

ES.6 Documented Illicit Chemical Discharges at Case Study Utilities

For the three case study utilities (OCWD, City of San Diego, and Singapore PUB), occurrence of any documented major chemical peak events was reviewed.

ES.6.1 Orange County Water District

In 2013, OCWD GWRS experienced an acetone peak event that has been described extensively in other reports. OCWD reported this occurrence to the California Regional Water Quality Control Board (RWQCB) shortly after the event. During this event, OCWD collected samples to investigate compound(s) responsible for the elevated TOC levels. A review of the resulting data revealed that acetone (only) was detected at elevated concentrations. OC San and OCWD were unable to determine the source of the 2013 acetone event. OCWD GWRS staff undertook a series of response actions following the event including developing updated RO permeate TOC response protocols (i.e., “investigate” or “shut down” response actions depending on elevated TOC value and duration).

Detailed analysis of the above 2013 acetone event was completed for the present study to estimate the theoretical mass (and volume) of chemical discharged to the sewershed, to have caused the TOC peak that was captured, based on several assumptions. From this analysis, the volume of acetone discharged to the sewer system is estimated to be ~1,900-9,500 gallons, or approximately up to two conventional tanker trucks of 5,000 gal each.

In 2018, OCWD GWRS detected two more chemical peaks. In 2018, dual TOC analyzers were in use, compared to just one set in 2013 on the RO feed and RO permeate. An increase in RO feed TOC was not apparent during both 2018 events, due to the lesser size of these peaks compared to that recorded in 2013, such that the baseline feed TOC “masked” the peak. Based on OCWD’s updated response protocols from 2013, OCWD staff collected grab samples during the elevated TOC events. For the 10/9/2018 event, samples were analyzed using the EPA 524.2 method and found to contain 215 µg/L of acetone in the RO permeate. At a later date, OCWD was informed about the unintentional discharge of 700 gallons of isopropyl alcohol by a local food and drug manufacturer due to a significant operator error that occurred the morning prior to the TOC spike. Isopropyl alcohol is readily used in the cleaning of food or pharmaceutical preparation equipment and can biologically oxidize to acetone. The manufacturer has since been directed to implement corrective actions to avoid future slug discharges of isopropyl alcohol. Detailed analysis completed for the present evaluation suggests that the size of the TOC peak corresponds to a volume of ~600 gallons of acetone (or ~590 gallons of isopropyl alcohol based on specific gravity ratios), which approaches the volume of isopropyl alcohol reported to have been discharged by the food and drug manufacturer. This is over an order of magnitude less than the discharge estimated for the 2013 event. For the 10/24/2018 event, investigative sampling again identified acetone. Unlike the earlier October 2018 event, the source for this event was not determined.

ES.6.2 City of San Diego

The City of San Diego (City) operates the 1 MGD Pure Water Demonstration Facility (PWDF) operational since 2011. The PWDF receives tertiary treated effluent from the North City Water Reclamation Plant (NCWRP) to produce highly-treated recycled water using a five-step water treatment process of ozonation (O_3), biological activated carbon filters (BAC), microfiltration (MF), reverse osmosis (RO) and ultraviolet disinfection with a chlorine based ultraviolet light advanced oxidation process (AOP).

Online monitoring shows that TOC in the RO permeate has consistently been under 0.1 mg/L. There have been two events where deviations in TOC were observed; one event was an RO permeate TOC decrease related to bringing the RO system back online after a several-month shutdown; the other was a slight increase in RO permeate TOC related to an artifact of the demonstration facility that would not occur in a full-scale facility.

The demonstration facility has undergone a number of challenge tests (intentional spiking of compounds into the feed), the findings of which are useful for the present study to evaluate treatment system robustness due to chemical peaks as well as the capability of TOC monitoring to observe these compounds. The challenge tests consisted of spiking neutral low molecular weight compounds known to be challenging for advanced treatment at the inlet of two treatment train configurations: O_3/BAC-MF/UF-RO-AOP and MF/UF-RO-AOP. The spiked compounds and influent concentrations of these compounds during these challenge tests were: 1,4-dioxane (907 µg/L), acetone (2,667 µg/L), formaldehyde (307 µg/L), and *N*-nitrosodimethylamine (NDMA) (550 µg/L).

For the O_3/BAC-MF/UF-RO-AOP system, the cumulative reduction of compounds was 99.5% for 1,4-dioxane, 66% for acetone, 93% for formaldehyde, and 99.5% for NDMA. The majority of the reduction of acetone and formaldehyde occurred during BAC, which suggests the effectiveness of biologically active barrier to control chemical peaks. When O_3/BAC was not included as pretreatment to MF/UF-RO-AOP, the cumulative reduction of compounds was lower, at 83% for 1,4-dioxane, 15% for acetone, 10% for formaldehyde, and 98.5% for NDMA.

Thus, for potable reuse treatment trains employing MF/UF-RO-AOP without O_3/BAC pretreatment, the theoretical maximum load concentration in the feed water – to be able to reduce concentrations via FAT to below relevant limits (for the tested compounds) – is considerably less. The addition of O_3/BAC as pretreatment to RO-AOP provided additional protection against all the spiked contaminants, indicating that increasing the robustness of treatment trains allows for handling of greater contaminant loading in events of chemical peaks (such as illicit chemical discharges).

In order to measure the effectiveness of the TOC analyzers in recovering the spiked compounds, a mass balance was performed using the measured TOC and compound concentrations. Overall, TOC recovery was within ± 15% relative to spiked compound concentration and background TOC, indicating that the TOC analyzers used successfully recovered the spiked compounds and clearly indicated the occurrence of a chemical peak.

ES.6.3 Singapore PUB

Currently, recycled water produced by PUB, known as NEWater, is mainly used in wafer fabrication plants, industrial estates, and commercial buildings for cooling and industrial processes. During dry periods, NEWater is added to PUB’s drinking water reservoirs to blend with raw water. There is a total of five NEWater plants which together feature a capacity of 175 MGD. PUB also owns four water reclamation plants (WRPs, i.e., wastewater treatment plants) which together have a total capacity of 360 MGD.

ES.6.3.1 Documented Illicit Chemical Discharges at JWRP

The Jurong Water Reclamation Plant (JWRP) catchment area has the highest presence of high-risk dischargers and is currently not serving a NEWater facility. In order to prevent and deter illicit chemical discharges in the JWRP catchment, PUB has employed close monitoring of high-risk dischargers through the installation of VOC monitoring units in the sewershed. The VOC monitoring units have auto-sampling capabilities and are useful for source tracing of illicit chemical discharges.

There are currently 10 VOC monitoring units in the JWRP catchment that are strategically located for source tracing of VOC illicit discharges. The installation of 32 additional VOC monitoring units in the JWRP catchment is planned. There has been a clear decrease in the number of high VOC incidents (e.g., >50 mg/L) in the JWRP catchment since the VOC monitoring units were installed. PUB has also confirmed that a reduction in the concentration of toluene and methylene chloride in the influent water has been attributed to the reduction of VOC-related incidents at JWRP.

As an example, during a May 2012 event, an alarm was triggered for a particular sewershed location reading an elevated VOC value; only one upstream collection system location was also showing an abnormal VOC value, indicating the general location of the discharge incident. In their first year of operation (2011-2012) of the VOC monitoring units, PUB received 20 alerts of high VOC incidents and was able to identify the source that discharged the chemicals into the public sewers for 18 of those cases.

ES.6.3.2 Documented Illicit Chemical Discharges at KNF

The Kranji NEWater facility (KNF) produces high-grade reclaimed water for both industrial and indirect potable reuse purposes. The treatment process train consists of MF, RO, and UV disinfection. The KNF has strict operating bounds with limits often more conservative than industrial customer specifications.

In 2017, the KNF experienced a high TOC incident that was ultimately found to be caused by the presence of N,N-dimethylacetamide (DMAc) in the RO permeate. The incident was indicated by a baseline shift of > 10 µg/L TOC in the RO permeate and a continuous uptrend. Samples were collected during this high TOC event for investigative purposes and GC-MS analysis identified the presence of DMAc, which is used by wafer fabricators for wafer cleaning. PUB followed up accordingly with the discharger involved.

In 2019, KNF experienced a high TOC event where acetone was identified as a cause. Based on lab sampling results, acetone (~270 µg/L) and methyl isobutyl ketone (~25 µg/L) were detected in the RO permeate samples on this day. Preliminary investigation indicated that the high TOC was caused by a company in the wafer cleaning industry. PUB followed up accordingly with the company involved.

ES.6.4 Common Features of Documented Chemical Peaks

In addition to meeting the criteria defined above to be classified as a chemical peak, the chemical peaks evaluated from the above case study utilities had the following characteristics:

1. Chemical peaks were caused by passage of neutral low molecular weight compounds. Acetone, in particular, was identified as the cause for chemical peaks across all three utilities. Acetone is the simplest and smallest ketone with a molecular weight of 58.08 g/mol.
2. TOC monitoring was effective for identifying the presence of neutral low molecular weight compounds in the RO permeate which caused the peaks. RO feed TOC analyzers were not as effective in capturing chemical peaks during low concentration peak events – likely due to masking and/or diurnality of the ambient feed TOC.

3. Peak TOC values were not instantaneously achieved during chemical peak events, suggesting dispersion and/or mixing of the discharged chemical or that the chemical was discharged in a step-feed (continuous) manner.
4. The decrease in TOC took longer than the increase in TOC during chemical peak events (i.e., the peaks appear to tail-off more slowly than they rise), suggesting that the reduction of chemical peaks takes longer than their increase to the peak value.

ES.7 Instrumentation to Monitor Chemical Peaks during Advanced Treatment

As noted previously, for this evaluation, chemical peaks are defined as abnormal events caused by the intentional or unintentional illicit discharge of chemical-containing waste streams, such that water quality monitoring of the treatment process deviates from baseline monitoring conditions. Since a source control-related grab sampling program would conduct monitoring of the DPR source water on only a monthly or quarterly basis, it cannot be expected to capture chemical peaks that only last hours to days. As such, a more frequent and more automated monitoring method for the advanced treatment process is desirable to capture chemical peak events.

To do so, this evaluation assumes the use of online TOC analyzers. TOC analysis is used to quantify the total amount of organic carbon contained in a sample by converting the organic compounds to a single form while excluding inorganic carbon from the analysis. For potable reuse applications, it is common practice to place TOC analyzers on the RO feed and RO permeate streams. TOC monitoring has been identified previously as a feasible option for capturing chemical pulses. In addition, TOC is often already used as a critical control point (CCP) monitoring device for RO systems related to compliance.

Though TOC is an industry-accepted method for monitoring RO performance and is used to detect chemical peaks, there are different methods of TOC analysis used in TOC analyzers available from different manufacturers. Some TOC methods may be more suitable for detecting chemical peaks, while others may underestimate the chemical content in the sample which would provide a false-negative. Discussion of TOC detection methods is provided in the report and experimentation was completed to evaluate the suitability of different commercially available TOC analyzers in terms of detecting and recovering the presence of spiked volatile organic compounds in two relevant potable reuse water matrices—reverse osmosis feed water and permeate. The experimentation study's report is included in Appendix A.

Current available and accepted methods for measurement of TOC in water, source water, and wastewater rely on accurate determination and/or removal of inorganic carbon, the process where there is the potential to lose some purgeable organics. Therefore, TOC methods commonly measure non-purgeable organic carbon (NPOC) as TOC. Almost all of the commercial TOC meters that were tested during this project showed excellent ability to measure NPOC as demonstrated by the system suitability testing and demonstrated acceptable performance of measurement of volatile organic compounds with Henry's Law dimensionless constant (H_{yc}) of less than or equal to 0.133 with at least 50% recovery. Purgeable organics are diverse in chemical properties including boiling point and vapor pressure, water solubility, miscibility with water, and purgeability. Detection of highly purgeable compounds ($H_{yc} > 0.2$) by TOC meters appears to be limited; however, the probability of such compounds to remain after upstream wastewater treatment at appreciable concentrations is low and of lesser concern due to their removal during aeration, limited water solubility and miscibility.

During the case study evaluations, VOC concentrations were evaluated to assess removal through the secondary aeration treatment process. While there was some variability between the two facilities, generally VOC removals in both cases increased for compounds with higher H_{yc}. For example, methylene chloride with H_{yc} of 0.133 was removed by 43.5%, while toluene with H_{yc} of 0.269 was removed by 94.1% and for compounds with H_{yc} higher than 0.308 a greater than 99.9% removal can be expected. Wastewater treatment facilities treating for BOD removal and achieving complete nitrification would be expected to achieve similar, or greater removal of VOCs with lower H_{yc} values, based on actual air to water ratios driven by the influent BOD and TKN loading. Therefore, the secondary treatment process, which includes both biological degradation and air stripping capacity provides an additional barrier of these types of organic compounds. Provided that the tested TOC meters showed at least 50% recovery for detection of compounds with H_{yc} up to 0.133, it is expected that current commercial TOC meters have the ability to detect chemical peaks originating from volatile organic compounds.

Source control programs from the case studies were effective at reducing the number and extent of chemical peaks observed by reclamation and advanced water purification facilities (Section 4.3). The observed performance is adequate for expected VOCs that may remain post-upstream wastewater aeration and biological processes and reverse osmosis filtration. Amongst the commercially available TOC meters that were tested during this project, at least two models demonstrated acceptable performance and are recommended for DPR projects.

ES.8 Chemical Peaks in Direct Potable Reuse Scenarios

In order for a chemical peak to escape well-functioning FAT, an abnormal event (i.e., illicit discharge) must take place. This project analyzed the impacts of variables surrounding the illicit discharge on chemical peak characteristics when the peak reaches the treatment facility and throughout treatment. Downstream of the AWTF, the amount of blending water available and mode of DPR (SWA, TDWA, etc.) significantly impacts the balance of source control, monitoring, treatment, and blending required to successfully “average” chemical peaks.

ES.8.1 Variables Impacting Chemical Peak Characteristics

With regard to an intentional or unintentional illicit discharge of a chemical into the sewershed, this study evaluated the impacts of variables surrounding the illicit discharge on chemical peak characteristics when the peak reaches the treatment facility and throughout treatment as follows:

1. **Sewershed size** – The size of the sewershed plays a role in “averaging” (i.e., dampening and diluting) a chemical peak since the sewershed can offer dilution and possible dispersion.
2. **Discharge volume** – The volume of chemical discharged to a sewershed will have a direct impact on the magnitude of a chemical peak. Figure ES-2 illustrates the impact of different discharge volumes within the same sewershed. A similar figure was developed for each of the key influences in the report (e.g., different sewershed sizes, discharge location, etc.).
3. **Discharge location** – The location of discharge will influence the magnitude and shape of a chemical peak due to dispersion of the peak that occurs within the sewershed as it travels to the WWTP and AWPF. A utility benefits from greater sewershed dispersion (i.e., illicit chemical discharges further away from the plant headworks) since a peak will be distributed over a longer period of time, lowering the maximum concentration observed and increasing the likelihood that sewershed monitoring captures the event (providing increased response time). A discharge occurring near or at the head of the WWTP would have a much higher peak maximum value, such that diversion or additional treatment may be required. This type of discharge would also have a much shorter duration.
4. **Discharge duration** – Considering an equal mass chemical discharge, the duration of the discharge will directly impact the shape of a peak. This occurs since there is greater dilution of a chemical as discharge duration increases for the same mass discharge.

5. **Treatment robustness** – Treatment robustness is the ability of a potable reuse system to address a broad variety of contaminants and resist catastrophic failures. In terms of chemical peaks, a robust treatment train is beneficial in that it can help abate the passage of compounds that would otherwise pass through.
6. **Blending** – Blending can offer "averaging" of chemical peaks if there is sufficient retention time in the blending system (e.g., tank, reservoir) to partially dilute a peak. Related to DPR applications, blending can be achieved by the addition of an engineered buffer or a "small reservoir" that does not meet SWA (surface water augmentation) requirements for dilution and therefore is not defined as SWA.

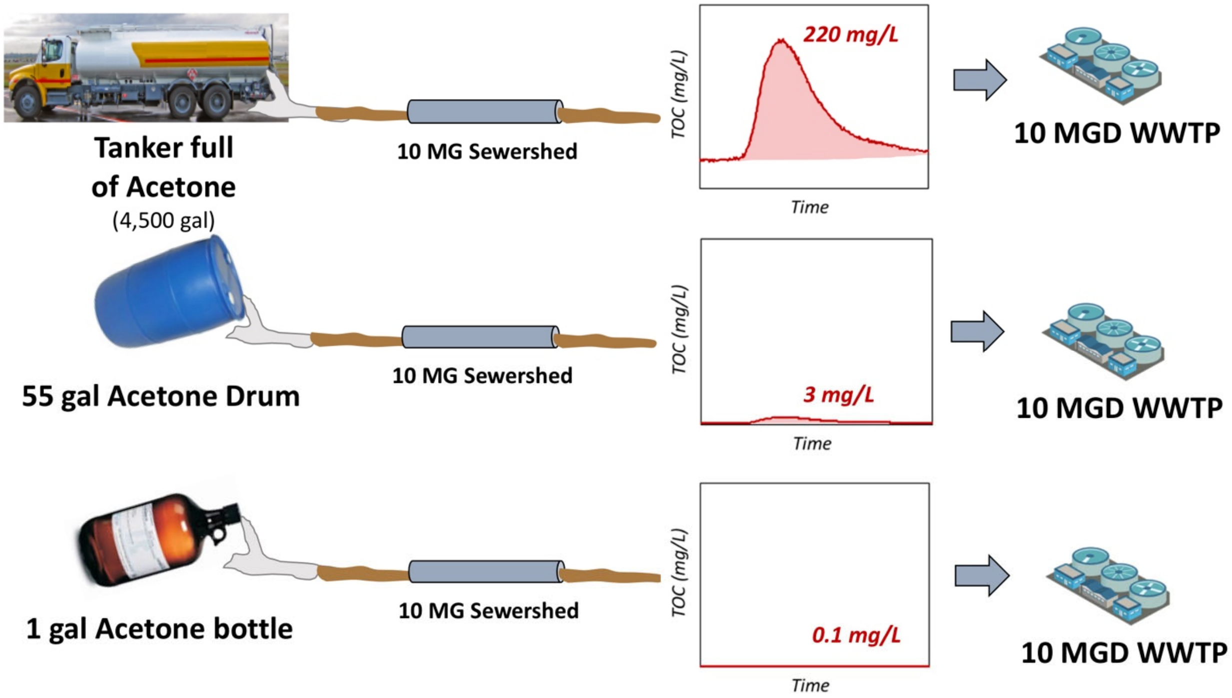

Figure ES-2. Impact of Discharge Volume for a Theoretical Illicit Chemical Discharge.

The influence of blending on chemical peak characteristics during a chemical peak event was evaluated in the present study via a continuously stirred tank reactor (CSTR) model developed to evaluate different sizes of a theoretical tank or reservoir that could be used for blending. The tank or reservoir is assumed to be located after the AWPF. The modeled tank scenarios only offered modest peak dilution. A tank with a retention time of 3 hours was not particularly effective in terms of peak "averaging", as the 5.7 mg/L TOC input resulted in a maximum tank effluent TOC concentration of 5.5 mg/L. A tank retention time of 24 hours offered a reduction of approximately 60% at 2.2 mg/L TOC in the tank effluent. As for the modeled reservoirs, a retention time of 10 days was sufficient to "average" the maximum concentration from 5.7 mg/L to 0.30 mg/L. In other words, a 10-day reservoir with ideal CSTR characteristics would be sufficient to dampen this worst case-scenario observed chemical peak to levels below those permissible per current indirect potable reuse for groundwater replenishment (i.e., TOC of 0.5 mg/L). The results suggest that blending can be effective at peak averaging when available and when sufficiently large; an advantage of blending over treatment is that it is non-selective to the chemical type. However, blending is not available for DPR scenarios that do not utilize an environmental or engineered buffer (i.e., raw water augmentation (RWA) with no buffer and treated drinking water augmentation (TDWA), discussed further below).

ES.9 Implications on Direct Potable Reuse Scenarios

The shift to DPR in the State of California can be characterized as the reduction (or elimination) of an environmental buffer between water purification and consumer distribution. An environmental buffer, consisting of a groundwater basin or a surface water reservoir, provides response time and in some cases an additional treatment barrier for a utility. Thus, the reduction or removal of that buffer requires greater control and assurance on the quality of advanced treated water.

This study evaluated the implications of chemical peaks for different DPR scenarios and how “averaging” (dampening) of such peaks can be achieved. The following DPR scenarios (Figure ES-3) were evaluated:

1. RWA with a “Small Reservoir”
2. RWA with an Engineered Buffer (Tank)
3. RWA without an Environmental or Engineered buffer
4. Treated Drinking Water Augmentation (TDWA)

Figure ES-3 provides a schematic of these DPR scenarios in terms of location of WWTP, AWTF, environmental buffer (when used), and drinking water treatment plant (DWTP).

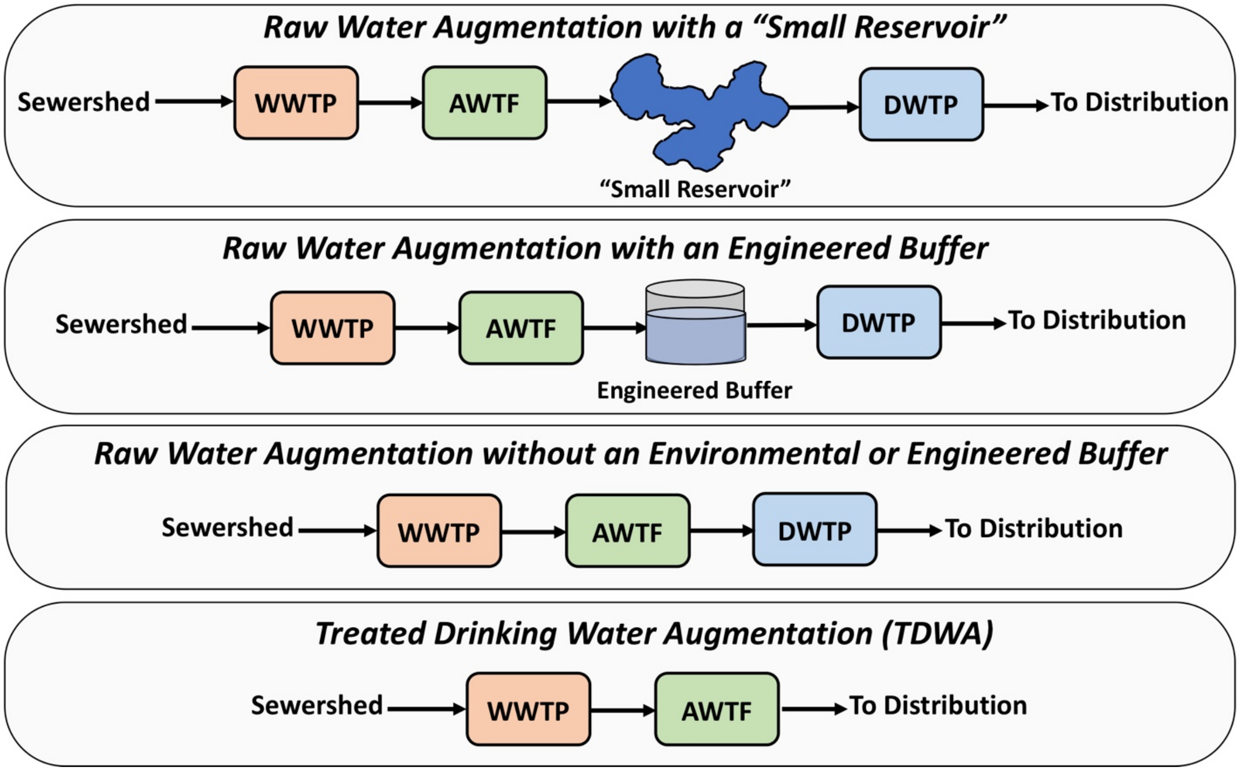

Figure ES-3. Schematic of DPR Scenarios.

For DPR scenarios, the “averaging” of a chemical peak will likely occur from a combination of source control, treatment, monitoring, and blending. This is illustrated in Figure ES-4. Treatment is achieved by the grouping of the WWTP, AWPF, and DWTP. Although the DWTP is mentioned, the WWTP and AWPF are considered the critical systems for chemical peak averaging since the DWTP is typically not designed for this purpose and therefore should not be relied upon by a DPR facility for chemical peak averaging.

Figure ES-4. Key Components and Their Function for Chemical Peak "Averaging."

The hypothetical fate of a chemical peak under each of the four DPR scenarios is discussed the report. In the latter two cases where there is no buffer, there is an increased need for enhanced source control, additional monitoring, and robust treatment to make up for the lack of a buffer that provides blending. Thus, the relative emphasis that should be placed on these peak "averaging" strategies differs for the above four different DPR scenarios.

Detailed programmatic (e.g., source control) and treatment system design is site-specific and was outside the scope of the present study. These would be included in the engineering design and feasibility review for a DPR facility in collaboration with the regulatory authority.

ES.10 Project Recommendations

This project is the fourth of five research projects supporting the California SWRCB to develop criteria and guidelines for DPR. The project evaluated the potential for certain chemicals to persist through advanced water treatment systems and options for the detection of such chemical peaks. It also developed criteria for differentiating chemical peaks from normal facility variations, and evaluated treatment and blending options. The project reviewed source control programs from case study utilities, evaluated TOC analyzers for VOC detection and quantification, discussed documented chemical peaks, and discussed implications of chemical peaks to different DPR scenarios.

Four key strategies are recommended that can be used to "average" chemical peaks: source control, monitoring, treatment, and blending. Because these strategies average chemical peaks in different ways, it is important to incorporate a balanced approach that fosters a reliable DPR implementation to control chemical peaks. Blending can be very effective at peak averaging when available and it is non-selective to the chemical type in doing so. However, blending is not available for DPR scenarios that do not utilize an environmental or engineered buffer. For such DPR scenarios, it is inherent that the remaining averaging strategies need to be enhanced. Additional treatment barriers in conjunction with

FAT should be considered to increase robustness in reducing the concentration of chemical constituents. Examples of such barriers include ozone/BAC pretreatment, air stripping, activated carbon, and additional RO/AOP treatment. Enhanced monitoring along with source control is also critical for DPR scenarios lacking an environmental or engineered buffer. These two components “average” peaks in an indirect manner, helping mitigate both the occurrence and magnitude of chemical peaks. These recommendations are included in the summary list below.

In summary, the project recommendations are:

1. A definition of a chemical peak (Chapter 3) is recommended to differentiate normal facility variation in water quality from true chemical peaks. In this study, chemical peaks are defined as resulting from intentional or unintentional illicit discharges of chemicals to the sewershed.
2. Online monitoring of TOC (Chapters 4 and 6) is recommended as a feasible option for capturing chemical peaks. TOC is already used as a critical control point (CCP) monitoring device for RO systems related to compliance.
3. Experimental results suggest that commercially available TOC analyzers have the ability to detect chemical peaks originating from volatile organic compounds (Chapter 6 and Appendix A). Amongst the TOC meters that were tested, at least two models demonstrated acceptable performance and are recommended for DPR projects.
4. Given that chemical peaks are expected to last on the order of hours to days, no more frequent than a fifteen minute minimum sampling interval is recommended for the online TOC analyzers (Chapter 3).
5. Due to the very limited expected frequency of chemical peaks (< 0.5% of case study data evaluated), periodic grab sampling (e.g., weekly, monthly, quarterly) for compounds known to potentially escape FAT is not recommended for DPR for the explicit purpose of discovering an illicit discharge (Chapters 3 and 4).
6. Utilities should prepare a formal TOC response protocol in the event of a TOC peak (Chapter 4). A tiered response protocol may be used to define actions taken depending on characteristics of the event (i.e., TOC concentration and duration). As part of a response protocol, grab sampling is recommended when a peak has been observed and confirmed by the TOC analyzers in an effort to identify the responsible chemical(s) and inform the source control program.
7. An enhanced source control program is recommended for DPR that proactively deters and diminishes the occurrence of chemical discharges (Chapter 4). A tailored source control monitoring program that is continually improved serves as a preventative measure for controlling peak events, and along with enhanced monitoring (e.g., sewershed, on-line, etc.) can help identify the source of an illicit discharge.
8. Additional treatment barriers in conjunction with FAT should be considered to increase robustness and further reduce the concentration of chemical constituents (Chapter 3). Examples of such barriers include ozone/BAC, air stripping, activated carbon, and additional RO and/or AOP.
9. DPR applications that have the option to use “small reservoirs” should consider doing so given the benefits of small reservoirs for chemical peak “averaging” (Chapter 5) due to blending.
10. Utilities considering DPR should pursue a balanced approach to control chemical peaks that includes an appropriate combination of two or more of the following: source control, enhanced monitoring, additional treatment barriers, and/or blending (Chapter 5).

CHAPTER 1

Introduction

The California Division of Drinking Water (DDW) of the State Water Resources Control Board (State Water Board; SWRCB) is charged with developing the regulations for direct potable reuse (DPR) projects in California. As part of California Senate Bill (SB 918), enacted in 2010, the state was required to convene an Expert Panel to study the technical and scientific issues associated with DPR and to advise the SWRCB on the feasibility of developing uniform water recycling criteria for DPR. At the conclusion of its investigation, the Expert Panel found development of such criteria feasible, such that the level of public health protection would be as good or better than existing potable water supplies (Olivieri et al. 2016).

In 2013, SB 322 additionally required the DPR Expert Panel to assess whether additional research was needed to establish DPR criteria. To address the knowledge gaps identified by the Expert Panel, six research projects were identified and funded by the SWRCB. This project is the fourth of the five research projects managed by The Water Research Foundation (WRF). This report serves to document the efforts and outcomes of the project’s Technical Working Group (TWG).

1.1 Potable Reuse

Water reuse is a droughtproof, reliable water resource that has been successfully incorporated into many communities in California. Water reuse can benefit a community by offsetting often more expensive imported surface waters, relieving stress on over-drafted groundwater basins, and/or reducing discharge to sensitive receiving waters (NRC 2012). In the case of non-potable reuse, implementation is challenged by the costly installation of an often-large secondary distribution system (i.e., purple pipe) within a community.

Indirect potable reuse (IPR), via groundwater replenishment, is currently a significant use of recycled water in California and has been occurring in the state since 1962 (NRC 2012). California groundwater replenishment regulations were adopted in 2014 and require that a retention time of at least two months be provided in the subsurface (i.e., environmental buffer) prior to extraction for potable purposes. However, many operating projects have ample retention times on a time-scale of years. The regulatory requirement for retention time is to allow the project sponsor ample response time to address any treatment failures and implement actions to ensure the protection of public health, although water quality benefits are often realized in the environmental buffer. In general, existing groundwater recharge projects are located where 1) there are large groundwater basins that provide significant retention times and 2) there is a need to inject water to prevent seawater intrusion. However, with new projects coming on-line in 2020 and into the future, it will be more common for retention times to be less than 1 year.

To expand water reuse in California, the State Water Board adopted surface water augmentation (SWA) regulations in 2018, another form of indirect potable reuse where a reservoir provides the environmental buffer and is in the process of developing regulations for DPR via raw water augmentation (RWA) and future regulations for treated drinking water augmentation (TDWA) will follow. Although reservoir augmentation via SWA is a form of indirect potable reuse, projects that do not meet the minimum hydraulic retention time requirements will be regulated as RWA, a form of DPR per California code. Assembly Bill 574 (AB 574) requires regulations to be developed for RWA by

December 31, 2023, and Table 1-1 indicates the general differences between these three modes of potable reuse (SWA, RWA, and TDWA). A commonality between these three modes of potable reuse is the reduction of the environmental buffer between water purification and consumer. An environmental buffer, consisting of a groundwater basin or a surface water reservoir, can provide treatment and response time for a utility. Thus, reduction or removal of that buffer requires greater controls on the quality of advanced treated water.

Table 1-1. Pending Potable Reuse Modes in California.

Mode of Potable Reuse	Receiving Water Body	Key Characteristics
Surface Water Augmentation (SWA)	Surface water impoundment prior to drinking water treatment plant (DWTP)	-Minimum of two months Hydraulic Retention Time (HRT) -Minimum dilution of 100:1 (or 10:1 when subjected to additional treatment) determined by a validated hydraulic model -Projects that do not meet HRT requirements are considered DPR -Final SWA Regulations adopted in 2018
Raw Water Augmentation (RWA)	Source water of DWTP	-Water will be blended and retreated in DWTP -Regulations to be promulgated by 2023
Treated Drinking Water Augmentation (TDWA)	Finished water distribution system	-No additional treatment beyond recycled water purification -Regulations likely to be developed after RWA

The Expert Panel identified key elements of a successful DPR program, which include a combination of:

1. Source control
2. Monitoring
3. Treatment
4. Blending

Source control includes establishing and enforcing industrial discharger limits and monitoring, as well as pretreatment requirements. With the expansion of potable reuse to more direct forms, the water industry must transition to view the sewershed as a parallel concept to a drinking source watershed with a focus on maintaining the highest quality source water for the DPR facility. Source control programs in existing IPR projects are discussed as part of Chapter 4.

Monitoring is a critical component to ensure reliability in DPR programs. Monitoring may play a role in every stage of the DPR cycle: detecting water quality changes in the sewershed, leaving the wastewater treatment plant (WWTP), between the advanced water treatment facility (AWTF) unit processes, and in final product waters, and empowering diversion of problematic water from the advanced water treatment plant.

On-line monitoring provides alerts and allows for response to a chemical peak occurrence, which in some instances can allow for source tracing. In such cases, on-line monitoring would serve to deter future chemical peaks from occurring. In this sense, on-line monitoring also serves as an *indirect* tool for "averaging" chemical peaks. On-line monitoring also provides peak characterization and, if coupled with a response action plan, allows identification of when concentrations exceed levels of concern.

Re-evaluating treatment strategies will be needed to meet water quality requirements for DPR. Blending options may include an environmental buffer of a reduced size to not be considered SWA, or be implemented with drinking water, raw water, or advanced treated water. In order to maximize the resilience of a DPR program, the relative contribution of these four elements- source control, monitoring, treatment, and blending- must be based on site-specific factors including treatment train process, water quality, availability of blending water, and diversion logistics. This concept is described in detail in Chapter 5.

Figure 1-1 highlights the function of each component relative to peak "averaging." Source control serves as an *indirect* tool (i.e., preventative) that prevents chemical peaks from occurring. An ideal source control program would completely eliminate the occurrence of chemical peaks, though realistically even the most effective program cannot achieve such goal.

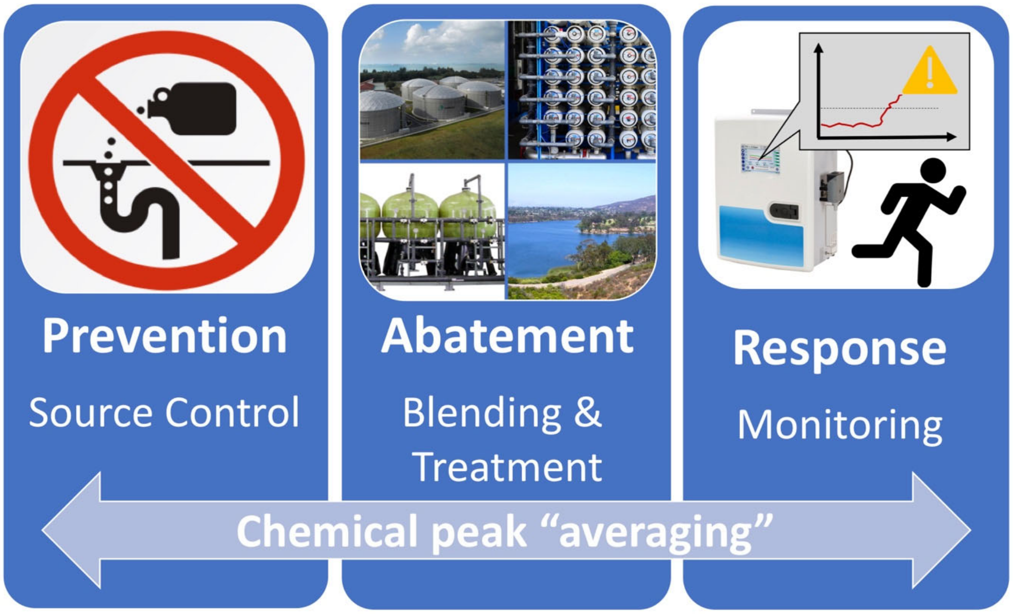

Figure 1-1. Key Components and Their Function for Chemical Peak "Averaging."

Blending and treatment serve as direct abatement of a chemical peak. Blending (through an engineered or environmental buffer) has a distinct advantage that it is non-selective and has the potential to reduce concentration of all chemicals equally. Effectiveness of treatment, on the other hand, is compound specific. A robust treatment train that targets compounds known to be challenging for removal across FAT can in some instances compensate for a lack of blending.

1.2 Chemicals in Wastewater and Potable Reuse

There are many thousands of chemicals that are used in commerce and may find their way into wastewater collection systems. The Chemical Abstract Service (CAS) compiles a database of regulated chemicals (CHEMLIST) from agencies around the world and contains over 394,000 chemicals. Through their normal uses, many of these compounds may enter the sewershed as domestic or industrial wastewater.

Conventional wastewater treatment can remove organic micropollutants via sorption to solids/sludge, biodegradation, volatilization during aeration, and/or oxidation during disinfection. While these mechanisms remove some micropollutants very efficiently, compounds resistant to these mechanisms can persist to the treated effluent (see Prasse et al. 2015 and references therein). Drewes et al. (2009) evaluated the removal of high production volume (HPV) household chemicals in biological wastewater treatment, either through conventional activated sludge or membrane bioreactor (MBR) processes. Of the 17 compounds measured in influent wastewater, 14 were removed at 80%-100% efficiency by both treatment processes. Regarding the other three compounds, less than 10% of bisphenol-A (BPA) and ~40% of *N,N'*-diethyl-*m*-toluamide (DEET) were removed by the MBR facility, while 3-indolebutyric acid (used in the fertilizer brand Miracle Gro™) was removed at ~60% by the conventional activated sludge facility. Overall, while wastewater treatment contributes to micropollutant removal, organic micropollutants routinely pass through the wastewater treatment process.

Full advanced treatment (FAT), although not mandatory for all potable reuse projects in California, is commonly employed and will likely be the centerpiece of any treatment train for near-term DPR projects in California. FAT consists of reverse osmosis (RO) followed by high dose ultraviolet (UV) light in conjunction with oxidant addition (e.g., hydrogen peroxide) to produce hydroxyl radicals (i.e., advanced oxidation processes; AOP). RO is typically preceded by low-pressure membrane filtration (i.e., microfiltration or ultrafiltration) to provide suitable feedwater quality for the RO process and provide additional pathogen and solids removal.

Although FAT does an excellent job of removing organic contaminants of concern, typically low levels (< 0.5 mg/L) of total organic carbon (TOC) persist in FAT product waters. It has been observed that larger compounds (MW > 200) and/or charged compounds are typically very well removed (>90%) by RO membranes (Drewes et al. 2006; Howe et al. 2019), and UV/AOP is an effective process to oxidize key contaminants (i.e., NDMA and 1,4-dioxane) and likely others that are not fully rejected by RO (Plumlee et al. 2008; Mestankova et al. 2016).

Short-duration chemical peaks have been observed in RO feed and RO permeate at a full-scale groundwater recharge facility (Olivieri et al. 2016) due to certain low molecular weight compounds that are not fully removed by FAT. These compounds were detected by an online TOC analyzer (Figure 1-2) that continuously monitors the RO permeate quality. Grab samples were collected in response to the peak for further investigation of the possible compound(s) responsible and it was determined to be mostly caused by acetone. This peak was likely eliminated biologically during soil aquifer treatment (after surface spreading) in addition to blending with groundwater (after surface spreading or injection) prior to well extraction; however, this event serves as a sentinel that even FAT is susceptible to some organics passing at significant concentrations with the right chemical specific properties (e.g., low molecular weight, uncharged, etc.). While the most probable cause for this chemical peak example is an illicit discharge, it will be important to include project barriers in DPR to ensure chemical peaks will be averaged through a combination of source control, monitoring, treatment, and blending.

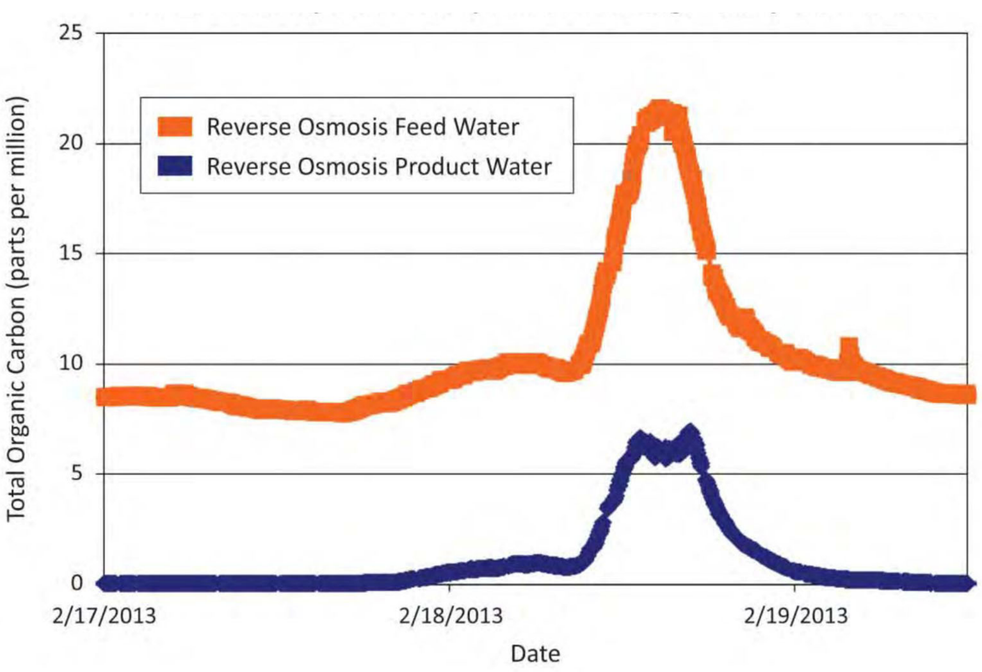

Figure 1-2. Chemical Peak at Orange County Water District's Full-Scale Potable Reuse Facility.
Source: Dadakis and Dunivin 2013.

1.3 Research Objectives

The objective of this work was to identify processes that can provide some "averaging" with respect to potential chemical peaks, particularly for chemicals that have the potential to persist through advanced water treatment. These processes are essential for the development of DPR criteria to continue to protect public health.

A literature review was conducted to identify chemicals and chemical families/groups that have the potential to persist through FAT (Chapter 2). Removal of these compounds with additional treatment technologies and strategies in addition to FAT was investigated.

Chapter 3 addresses the definition of a chemical peak, which is critical for peak identification in real-time by operators as well as post-event assessment. Mathematical guidelines are presented for the determination of baseline conditions at a facility. Guidelines were developed for determining if deviations from this baseline (i.e., higher RO permeate TOC) indicate the presence of a chemical peak to limit the number of false positive readings resulting in unnecessary operator response.

Source control and monitoring play a key role in the averaging of chemical peaks. Case studies of source control programs and monitoring practices at existing indirect potable reuse facilities are summarized in Chapter 4. Documented chemical peak events at these facilities are reviewed.

Chapter 5 investigates the impacts of variables surrounding an illicit discharge on chemical peak characteristics. The implications of the availability of blending water and mode of DPR (SWA, TDWA, etc.) on the relative contribution of source control, monitoring, treatment, and blending required to successfully "average" chemical peaks are discussed.

Online TOC measurement of RO permeate plays a key role in the detection of chemical peaks. Laboratory work was conducted to investigate the ability of commercially available TOC analyzers to detect chemicals that may persist through FAT. Compounds with a range of volatility and oxidation potential were evaluated, and results presented in Chapter 6.

The final chapter, Chapter 7, summarizes the study and provides recommendations for next steps and implementation.

CHAPTER 2

Literature Review

2.1 Chemical Removal by FAT

The FAT process train in California is defined by regulation as:

1. Reverse Osmosis
2. Advanced Oxidation Process

Membrane filtration (i.e., microfiltration or ultrafiltration), typically precedes the RO process to provide suitable feedwater and plays a critical role in achieving pathogen removal requirements but plays a negligible role in chemical removal. This multibarrier approach associated with FAT has been adopted to protect public health in potable reuse applications throughout the world. Challenge testing prior to startup, selection of appropriate surrogates, establishing critical control points, and online monitoring is used to ensure that system performance achieves operational and regulatory criteria under normal operating conditions, including diurnal and seasonal variations in influent quality. FAT systems have been proven to remove constituents of emerging concern (CECs) under such normal circumstances. The purpose of this evaluation is to identify known chemicals that could potentially challenge the FAT treatment train.

2.1.1 Reverse Osmosis

Rejection of constituents in water by RO membranes occurs mainly through three mechanisms: 1) electrostatic repulsion and/or Donnan exclusion, 2) adsorption, either onto the membrane surface or within the membrane structure, and 3) size exclusion. Details of these mechanisms can be found elsewhere (Bellona et al. 2004, Verliefde 2008). Due to rejection by these three mechanisms, the most likely compounds to have low rejection by RO membranes are 1) uncharged, 2) hydrophilic and/or polar, 3) low molecular weight (LMW) compounds. This general trend is reported extensively throughout the literature (Bellona et al. 2004, Yoon and Lueptow 2005, Drewes et al. 2006, and Yangali-Quintanilla et al. 2009).

Numerous studies have been conducted investigating rejection of organic compounds by RO membranes (Bellona et al. 2004, Yoon and Lueptow 2005, Drewes et al. 2006, Yangali-Quintanilla et al. 2009, and references within). These studies utilize different membranes developed by various membrane manufacturers, variability in testing waters (i.e., TOC and TDS levels), virgin versus used membranes, and variability in experimental size (i.e., bench-, pilot- or full-scale), making quantitative comparisons between studies difficult. Additionally, the high rejection of many organic compounds often leads to concentrations in the RO permeate below the detection limit, preventing accurate determination of rejection percentages. Thus, to describe overall trends while accounting for experimental variation, compounds in this study were grouped into chemical families and “binned” based on rejection percentage:

1. Good (>90%)
2. Intermediate (50-90%)
3. Poor (<50%)

Below are summaries of select key studies including relevant findings. These studies utilized paired sampling (simultaneous RO feed and RO permeate) in order to calculate rejection percentages, and span a wide range of chemical families.

Pharmaceuticals and personal care products (PPCPs) as well as pesticides are CECs commonly detected in treated wastewater effluent. The chemical composition of these compounds is highly variable, although the majority have characteristics that promote rejection by RO. Snyder et al. (2007a) conducted pilot studies evaluating removal of CECs in various treatment configurations and source waters, summarized in Table 2-1.

Table 2-1. CEC Rejection in RO Studies.

Source: Data from Snyder et al. 2007a.

Test Condition	Source Water	CECs Detected in RO Feed	CECs Detected in RO Permeate	CEC Rejection
2-stage RO, virgin membranes	Saline groundwater	18 (spiked)	Caffeine	85%
			Pentoxifylline	90%
2-stage RO, fouled membranes	Saline groundwater	18 (spiked)	Iopromide	46%
2-stage RO	Tertiary WWTP effluent, pretreated with UF	17	Iopromide	98%
			Sulfamethoxazole	98%
2-stage RO	MBR Effluent, pretreated with UF	18	DEET	95%
			Meprobamate	99%
			TCEP	97%
2-stage RO	MBR Effluent, pretreated with UF	20	TCEP[1]	91%
2-stage RO	Tertiary WWTP effluent, pretreated with MF	14	DEET	96%
			TCEP	98%
RO, full scale	Tertiary WWTP effluent, pretreated with MF	22	DEET	>99%
			Galaxolide	99%
			Gemfibrozil	>99%
			Naproxen	>99%
			Oxybenzone	92%
			Sulfamethoxazole	>99%
			TCEP	98%
Double Pass RO, full scale	Secondary WWTP effluent (non-disinfected), pretreated with MF	21	Caffeine	>99%
			TCEP	>99%

[1] Previous sampling event had no detectable TCEP (>94% rejection)

MBR = membrane bioreactor, MF=microfiltration, UF = ultrafiltration

In all studies utilizing wastewater as a source water for the treatment trains, micropollutant rejection by RO was greater than 90% for compounds detected both in the RO feed and permeate. Two compounds in spiked saline groundwater tests were detected in RO permeate with less than 90% removal: caffeine had 85% rejection in spiked saline groundwater utilizing virgin membranes, and iopromide had 46% rejection in spiked saline groundwater utilizing fouled membranes. Notably, both of these compounds were found to have >98% removal in other test conditions.

Rodriguez et al. (2012) tracked the concentrations of 61 volatile organic compounds (VOCs) through two reuse facilities treating secondary treated WWTP effluent with microfiltration (MF) and RO. VOC concentrations were highest in MF filtrate, due to disinfection byproduct (DBP) formation during chloramination (for biofouling control of MF and RO membranes) and/or exposure to the atmosphere, as one facility was located adjacent to an oil refinery. VOC rejection by RO from paired sampling events are shown in Table 2-2.

Table 2-2. RO Rejection of VOCs at Two Treatment Plants.

Source: Data from Rodriguez et al. 2012.

Chemical Family	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
Alkylbenzenes	Most C_8+	C_6-C_8; p-isopropyltoluene	
Haloalkanes		Chloroethane; Chloromethane; Trichlorofluoromethane	Bromomethane
Haloalkenes	Ethenes with 3-4 Cl atoms	Haloalkenes with 2 Cl atoms	
Halobenzenes		Most dichlorobenzenes	

Howe et al. (2019) analyzed data from ten years' worth of sample collection by the Orange County Water District (OCWD) for their Groundwater Replenishment System (GWRS) RO facility. Out of 365 chemicals analyzed, only 57 compounds were detected in the RO feed water on one or more occasion, and 25 compounds were detected in the RO permeate at least once.

Of note, methylisothiocyanate (MITC) was detected in 96% of RO permeate samples (n=187). MITC is a breakdown product of the herbicides dazomet and metam sodium, the latter of which is used in agriculture as well as to prevent vegetative growth in sewer systems. The high occurrence of MITC may indicate use of this herbicide within the Orange County Sanitation District (OC San) collection system. The antimicrobial triclosan was also detected in every RO permeate sample in which it was analyzed for (n=16; average RO rejection = 92%), although this is likely due to leaching from the membranes, which may have been treated with the chemical to prevent biofouling (Howe et al. 2019). Table 2-3 shows removal percentages of compounds with paired sampling:

Table 2-3. RO Rejection of Paired Samples at Orange County Water District.

Source: Data from Howe et al. 2019.

Chemical Family	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
PPCPs	Most PPCPs	Bisphenol A[1]	
Pesticides/Herbicides	Diuron		MITC
LMW oxygenated compounds		Formaldehyde; Acetone	
VOCs			Methylene Chloride

[1] Only one paired sample; identified by authors as potential outlier.

Howe et al. (2019) performed a detailed study of LMW compounds, including isomers and congeners, to evaluate the impact of functional chemistry on rejection across various membranes. The effects of functional chemistry, such as substituting a halogen for a methyl group, sheds light on why deviations are seen from the overall observed trends of higher rejection across the membrane for compounds with increasing molecular weight, charge, and hydrophobicity. Key findings from the study are presented in Table 2-4.

Table 2-4. Factors Affecting Organic Compound Rejection by RO.

Source: Data from Howe et al. 2019.

Factors Positively Correlated with Rejection	Functional Chemistry That Increases Rejection	Functional Chemistry That Reduces Rejection	Factors with Little Effect on Rejection
• Molecular Weight • Charge • Molecule size (radius, width, etc.) • log K_{ow}	• Increasing carbon chain length • Increasing number of functional groups • Increased branching • Functional groups close together (sterics)	• Replacing methyl groups with halogens • Carbon-carbon double bonds • Replacing hydroxyl groups with carbonyl groups	• Replacing Cl with Br

While Howe et al. (2019) evaluated the impact of various functional groups on rejection by RO membranes, the effect of heteroatoms (sulfur and nitrogen) on membrane rejection remains poorly studied. Fujioka et al. (2019) found that with N-nitrosamines, increasing the nitrogen content in the molecules decreased the rejection, possibly due to interactions with the membrane surface. Overall, additional research is needed to understand the effects of heteroatom presence on RO rejection.

Data from the above studies and additional work were compiled. A summary of the rejection by RO of various chemical families is presented in Table 2-5. Compounds that are charged, high molecular weight, or not commonly found in wastewater are not necessarily presented due to lack of available research. While DBPs are not typically of concern from an illicit discharge perspective, these compounds are included for completeness.

Table 2-5. Summary of RO Rejection of Organic Compounds and Chemical Families.

Chemical Family	Sub-group	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
VOCs	Solvents and Industrial Compounds	Ethers	Halobenzenes; 1,1,2-TCE	Nitriles; Haloalkenes Benzotriazole
	Haloalkanes	CCl_4; Ethanes with 3-4 Cl atoms; Most C_4+ haloalkanes	Some C_1-C_3 haloalkanes	C_1-C_2 haloalkanes with 1-2 halogen atoms
	Alkylbenzenes	C_{10+}	C_6-C_9	
	Pesticides/ Herbicides	1,2,3-TCP		MITC
LMW Oxygenated Compounds	Alcohols	Branched C_{4+} alcohols	Isopropyl alcohol; Most unbranched alcohols	Methanol; Ethanol;
	Aldehydes, Ketones	Methyl isobutyl ketone (MIBK)	Acetone; Unbranched C_3-C_6 Ketones	Formaldehyde; C_1-C_6 Aldehydes
PPCPs	Flame Retardants	Chlorophosphates; PFAS		
	Pharmaceuticals	Steroids; β-blockers; NSAIDs; X-ray Contrast Media		
DBPs	Nitrosamines	C_{4+} nitrosamines; NMOR	NDMA; NDEA	
	Halogenated DBPs	HAAs	HANs	THMs

References: Howe et al. 2019, Zeng et al. 2016, Rodriguez et al. 2012, Snyder et al. 2007a, Kiso et al. 2011, Tackaert et al. 2019, Fujioka et al. 2012; Doederer et al. 2014; Alotaibi et al. 2015

VOCs are among the most prone chemical families to have low rejection across RO membranes, as the functional chemistry that makes them volatile (low molecular weight, uncharged, etc.) allows for passage through the membrane. These compounds include haloalkanes, haloalkenes, halobenzenes, alkylbenzenes, and LMW oxygenated compounds.

In general, rejection of the broadly-defined PPCPs exceeds 1-log and often 2- log removal during paired sampling. Concentrations of the majority of PPCPs tested are below their respective detection limits in RO permeate, in which cases rejection percentage cannot be exactly quantified (but can be estimated as equal to or above a rejection percentage calculated using the detection limit, e.g., ≥90%); however, PPCPs such as gemfibrozil and sulfamethoxazole had at least 3-log removal in Snyder et al. (2007a).

While detection of PPCPs in RO permeate is not uncommon, measured concentrations are often near the detection limit, from 1-10 ng/L.

As mentioned above, DBPs are not considered constituents of concern from the perspective of a chemical peak caused by an illicit discharge in the collection system, which is the scope of the present study, as very few DBPs are produced industrially in high volumes. The low concentrations of disinfectants routinely used in treatment facilities also makes the production of a large DBP in the facility unlikely, even if a precursor compound came in as a chemical peak. Nevertheless, DBP removal by RO is summarized in Table 2-5. Select halogenated and non-halogenated oxidation disinfection byproducts have lower rejection across RO membranes (<1 log removal).

2.1.2 Advanced Oxidation Processes

AOPs are processes that utilize hydroxyl radicals to oxidize organic and inorganic contaminants that may be present in the RO permeate. UV/AOP performs oxidation via ultraviolet radiation coupled with the addition of an oxidant species such as hydrogen peroxide, ozone, or chlorine to form hydroxyl radicals. The ultraviolet radiation is applied with low-, medium-, or high-pressure lamps emitting either 185 nm or 254 nm radiation. Of these combinations, the use of low pressure 254 nm lamps is most common due to commercial availability and operating costs.

In order for direct UV photolysis (which is the process of breaking chemical bonds by light) of CECs to occur, the CEC must be able to absorb UV light, which typically requires electron densities such as those found in aromatic structures. While there are compounds that pass through RO and also absorb UV radiation, the majority of removal is achieved via reactions with hydroxyl radicals and other radical species during AOP.

Ozonation with chemical addition such as hydrogen peroxide is another common AOP utilized in water reuse. Ozone is a strong oxidant, but selectively oxidizes compounds with functional groups such as olefins, aliphatic amines, aromatic, and sulfur-containing moieties (Hubner et al. 2015). In RO permeate, the addition of hydrogen peroxide is used to generate significant concentrations of hydroxyl radicals due to the low TOC and alkalinity concentrations.

Ahmed et al. (2017) compiled data from over 100 studies on the degradation of PPCPs and pesticides utilizing multiple AOP systems. Data from UV- and ozone- based studies are summarized in Table 2-6. The use of hydrogen peroxide in both UV- and ozone- based AOP systems can be optimized to result in greater than 90% removal of pharmaceuticals and pesticides, while the processes without hydrogen peroxide show decreased removal efficiency of these compounds, emphasizing the importance of hydroxyl radical production. The FAT process train, with greater than 90% rejection by RO membranes and greater than 90% removal by AOP, thus provides robust protection from peaks of PPCPs and pesticides.

While industrial compounds, including VOCs, have poorer rejection by RO than PPCPs, these compounds are less studied in AOP systems, as they are often efficiently removed during conventional wastewater treatment. In order to evaluate potential removal of these compounds in full scale systems, reaction rate constants between target compounds and hydroxyl radicals were compared to the rate constant between hydroxyl radicals and 1,4-dioxane. Challenge testing of AOP processes are often performed by measuring the degradation of 1,4-dioxane, with a regulatory requirement of a minimum 0.5 log (69%) removal. Compounds identified to potentially persist through RO treatment were therefore classified as having good removal during AOP (>1,4-dioxane) or poor removal during AOP (<1,4-dioxane) in Table 2-7. Where available, removal percentages observed in various studies were also utilized.

Table 2-6. AOP Degradation of Pharmaceuticals and Pesticides.

Source: Data from Ahmed et al. 2017.

AOP Process	Good (>90%)	Intermediate (50-90%)	Poor (<50%)
Ozone	EDCs; Analgesics; Antibiotics; Anti-inflammatory; Lipid Regulators; Pharmaceuticals (other)	Pesticides; β-blockers;	
Ozone/H_2O_2	EDCs; Pesticides; Analgesics; Antibiotics; Anti-inflammatory; β-blockers; Lipid Regulators; Pharmaceuticals (other)		
UV		EDCs; Pesticides; Analgesics; Antibiotics; Anti-inflammatory; Pharmaceuticals (other)	β-blockers; Lipid Regulators
UV/H_2O_2	EDCs; Pesticides; Analgesics; Antibiotics; Anti-inflammatory; β-blockers; Lipid Regulators; Pharmaceuticals (other)		

Notes: EDCs = endocrine disrupting compounds

Table 2-7. Predicted Removal via AOP for Organic Compounds That May Persist through RO.

Family	Greater than 1,4-dioxane	Less than 1,4-dioxane
VOCs	Haloalkenes Halobenzenes Alkylbenzenes C_4+ Alcohols C_4+ Aldehydes C_6+ Ketones Acrylonitrile Benzotriazole	C_1-C_3 Haloalkanes C_1-C_3 Alcohols C_1-C_3 Aldehydes C_3-C_5 Ketones Acetonitrile MITC
PPCPs	Most pharmaceuticals	Flame Retardants
DBPs	Nitrosamines[1]	THMs

Notes: [1] High removal in UV/AOP systems

References: Drewes et al. 2008, Howe et al. 2019, Ahmed et al. 2017, Drewes et al. 2006, Buxton et al. 1988, Swancutt et al. 2010; Bahnmüller et al. 2015

As discussed above, AOP is most effective at removing compounds containing electron-rich moieties such as aromatic structures. Compounds not efficiently removed by AOP that also have poor to intermediate rejection by RO include LMW haloalkanes, trihalomethanes, and LMW oxygenated compounds (i.e., aldehydes, ketones, and alcohols).

2.1.3 Summary of Organic Compound Removal by FAT

The following chemical families were identified as having intermediate to poor rejection by RO membranes and poor removal by AOP (less efficient than 1,4-dioxane):

1. LMW haloalkanes
2. LMW alcohols, aldehydes, and ketones
3. Acetonitrile
4. MITC
5. THMs

Industrial use of solvents including LMW haloalkanes, alcohols, aldehydes, ketones, and acetonitrile make these the compounds with the highest potential to comprise a chemical peak persisting through FAT. LMW alcohols, ketones, and aldehydes can also be biologically produced within the WWTP. For example, a 2018 reported spill of isopropyl alcohol into the OC San collection system was the likely cause of a corresponding spike of acetone seen at the OCWD GWRS RO facility, measured via online TOC monitoring that prompted grab sampling, as isopropyl alcohol can oxidize to acetone under certain conditions (see Chapter 4). Similarly, MITC is a breakdown product of an herbicide used for control of vegetation in sewer systems and could potentially persist through FAT. Trihalomethanes have much lower production volumes, with chloroform being the most likely to be discharged into the collection system.

2.2 Additional Barriers for Peak "Averaging"

The established FAT treatment train provides a robust multi-barrier approach for the removal of pathogens and chemical contaminants from water. However, LMW chemicals have been documented to pass through FAT facilities during rare events (i.e., illicit discharges) and known chemical families have been identified which could pass through FAT if present in high enough concentrations. The following section will discuss additional barriers that are able to provide some reduction or averaging of chemical peaks.

2.2.1 Ozone/BAC as a Pretreatment

Ozonation results in the breakdown of large organic molecules, and the produced LMW organic compounds, including LMW aldehydes and ketones, can more easily pass through RO, increasing permeate TOC. The use of a biological process such as biological activated carbon (BAC) or sand filtration (which develops an attached growth biofilm) can remove a portion of these LMW compounds, as they are often more readily biodegradable than their larger precursors (Weinberg et al. 1993).

A potential issue with utilizing a biological process for the prevention of peaks is that many biological organisms require an acclimation period to be able to efficiently remove specific constituents. The microorganisms in a biologically active filter that has a relatively stable influent water quality (i.e., relatively constant food supply) will become dominated by organisms best suited to metabolize the constituents present in that influent stream. An atypical chemical peak may therefore not be efficiently metabolized by the microorganisms present in the filter. However, the microorganisms in the BAC of an ozone/BAC system would likely be exposed to a constant, fairly stable stream of LMW alcohols, aldehydes, and ketones produced by ozonation of organic matter, and may therefore be well suited to degrade a chemical peak of these compounds. Biological removal of formaldehyde and acetone in BAC following ozonation has been shown to reach 97% and 50%, respectively (Tackaert et al. 2019). To date, it has not been documented as to how much acetonitrile or MITC removal would occur as concentrations may not be effectively reduced if they are not as commonly found in the wastewater.

Destruction of organic compounds by ozonation occurs through similar mechanisms as the reactions with hydroxyl radicals, but the selectivity of ozonation results in reduced destruction of organics compared to oxidation by hydroxyl radicals in AOPs (Table 2-6). Due to the similar reaction mechanisms, ozone would not provide an efficient additional barrier if located directly after another AOP process.

Additionally, the low TOC present in RO permeate may not provide sufficient carbon to support biological growth in the BAC process if located after RO and AOP. Thus, if ozone/BAC were to be used as part of an AWTF treatment train with the goal of peak reduction, it would be best located prior to MF/RO.

Additional benefits of ozone/BAC pretreatment are the availability of established surrogates that can be used to ensure process performance for disinfection and chemical peak averaging. For ozone, ozone residual is commonly used in water treatment facilities for disinfection and changes in the UV transmittance (UVT) have been documented to correlate with CEC removal with ozonation (Gerrity et al. 2012). For the BAC process, the removal of TOC and UVT can provide operations and regulators with the assurance that the biology is active and providing the intended chemical treatment.

2.2.2 Air Stripping

Air stripping is a treatment technology utilized to remove volatile compounds from water. Air stripping technologies range in complexity from spray nozzles, which aerosolize water droplets and increase VOC volatilization, to packaged aeration strippers designed for VOC reduction.

Packed tower aeration (PTA) is a form of air stripping recognized by the California SWRCB DDW as a best available technology for the treatment of many VOCs. The water stream is pumped to the top of the tower, where it flows down over fixed media with large interstitial spaces. Blowers force air from the bottom of the tower in a counter flow to the water, stripping VOCs and exiting the top of the tower. Granular activated carbon (GAC) filters or other filtration media can be utilized to capture the stripped VOCs if required. While other air stripping technologies are used in the treatment of drinking water, PTA will be used as an example of compounds that can be removed from water via air stripping.

The Henry's Law constant (H_{yc}) describes the partitioning of a chemical compound between the aqueous and gaseous phases. This value is therefore used to determine the feasibility of removing a compound from water via air stripping. The US EPA classifies compounds with a H_{yc} (dimensionless) greater than 0.01 as amenable to air stripping via PTA, which corresponds to complete removal at an air to water ratio (A:W) of 100:1. Compounds with the potential to persist through FAT were therefore classified as having efficient removal via PTA if their respective Henry's Law constants (at 10°C; Knappe 2017) were greater than 0.01 (Table 2-8).

Typically, air stripping is employed in water treatment for the removal of a known contaminant and quantification of removal is used to establish operational performance. Due to the unknown nature of a potential chemical peak, an air stripping system could be designed to remove compounds with an H_{yc} above a baseline value, such as 0.01 as described above. Removal of disinfection byproducts such as THMs that are present in most FAT product waters could be used to measure performance of an air stripping system.

Decarbonation towers are utilized by some water reuse facilities to remove excess inorganic carbon from the product water. These towers are essentially PTA systems and could provide removal of volatile constituents. Aeration towers could also introduce contamination from biological growth and/or exposure to airborne contaminants.

2.2.3 Activated Carbon

GAC and powdered activated carbon (PAC) remove organic constituents primarily through adsorptive processes. GAC/PAC is effective at adsorbing many of the compounds that can be treated with PTA, which is why it is often used to treat PTA waste air streams. GAC/PAC can remove compounds from non-polar to intermediate polarity, but highly polar volatile compounds have reduced GAC removal efficiencies (Prasse et al. 2015).

Table 2-8 summarizes the removal of compounds identified to potentially pass through FAT via air stripping (PTA) and GAC/PAC.

Table 2-8. Removal of Compounds with Potential to Pass through FAT via Air Stripping and Activated Carbon.

Efficient Removal via GAC/PAC	Efficient Removal via GAC/PAC and PTA	Efficient Removal via PTA	Not efficiently removed by either
Hexachlorobenzene	Alkylbenzenes	Methylene Chloride	C_1-C_3 Alcohols
	Halobenzenes		C_1-C_3 Aldehydes
	Haloalkanes		C_3-C_5 Ketones
	Haloalkenes		Acetonitrile
	THMs		MITC[1]

[1] Potential removal by GAC/PAC; requires further testing

References: Staudinger and Roberts 2001; Knappe 2017; Worthington and Wade 2007; Kempisty et al. 2019

LMW alcohols, aldehydes, ketones, and acetonitrile are not efficiently removed by PTA or GAC/PAC. This is because while these compounds are volatile, they are highly miscible in water due to their polarity. Therefore, the TOC peak event shown in Figure 1-2 that was attributed to acetone would likely not have been addressed via the conventional use of GAC/PAC or PTA. While removal efficiency for these compounds is low, removal percentage can be improved with increased contact time (GAC/PAC) or tower height (PTA).

While serving to enhance the robustness of the FAT train, GAC treatment of RO permeate presents a challenge in identifying a meaningful surrogate to ensure performance. Treatment plants, such as the City of Oceanside's Mission Basin Groundwater Facility, do treat RO permeate with GAC. However, as discussed with air stripping, the performance is ensured by monitoring the removal of a specific chemical contaminant, 1,2,3-trichloropropane. Since this contaminant is commonly detected in the Facility's RO permeate, it can be used to determine when the GAC is no longer effective and needs replacement. As with air stripping, the unknown nature of a potential chemical peak requires design criteria of the GAC system to be conservatively set, possibly resulting in over-sized vessels.

2.2.4 Additional RO/AOP Treatment

While the use of additional RO or additional AOP processes does not increase the robustness (i.e., diversity) of a treatment system, increased removal of chemicals can be achieved. Some facilities may include additional RO to achieve specific water quality goals, such as boron or nitrogen requirements. The second pass RO treatment occurs by passing the RO permeate through an additional RO treatment train. While compounds with poor to intermediate RO rejection will have similar rejection through the second pass, the total rejection will increase and good removal (>90%) of some compounds, such as some haloalkanes, C_4+ ketones, and propanols, could be achieved.

As mentioned above, the use of additional AOP could be utilized to provide increased chemical removal. Similar to RO, while comparable removal would occur in the second AOP process, the additive removal would provide some benefit. Alternatively, additional RO and AOP treatment can be obtained through recirculation under certain circumstances, in which product water would be sent back through the same equipment again during peak events. Existing IPR facilities in Monterey, California and Singapore were designed to incorporate such recirculation options to provide additional treatment if needed prior to discharge.

2.2.5 Blending

The use of blending for the “averaging” of chemical peaks has the distinct advantage that it is non-selective, and has the potential to reduce concentrations of all chemicals equally. To achieve blending of chemical peaks, an additional water source is required. This can be DPR water that passes through the AWTF before and/or after the chemical peak, a raw water during RWA or a finished drinking water during TDWA. Blending can occur in an engineered storage tank, in an impoundment, or within transmission piping. Although blending is straightforward with regards to reducing a chemical peak, it should be noted that blending of advanced treated water with raw or treated drinking waters can have deleterious effects on corrosion and/or water treatment: reduced hardness and alkalinity in the advanced treated water can increase corrosion in the distribution system, and reduced alkalinity and turbidity can disrupt conventional coagulation/processes (Salveson 2018).

2.2.6 Summary

The established full advanced treatment train utilized for indirect potable reuse provides multibarrier protection and effectively removes contaminants including CECs under normal operating conditions. However, it is possible that the following chemicals could potentially persist through FAT, if present in high enough concentrations:

1. LMW haloalkanes
2. LMW alcohols, aldehydes, and ketones
3. Acetonitrile
4. MITC
5. THMs

In the event that a chemical peak is detected, a relatively small number of analytical methods are required to identify the compounds identified in this study. EPA Method 524.2 includes LMW haloalkanes and THMs. LMW alcohols and ketones can be quantified with EPA Method 8015D, and LMW aldehydes with EPA Method 8315A. Acetonitrile and MITC can be quantified with Method 8260B.

Additional barriers that could be used in conjunction with FAT to abate or average chemical peaks include:

1. Ozone/BAC Pretreatment
2. Air Stripping
3. Activated Carbon
4. Additional RO/AOP treatment
5. Blending

Site-specific factors will inform the relative contribution of source control, monitoring, treatment, and blending needed to provide reliability and resilience in a DPR program.

CHAPTER 3

Defining a Chemical Peak

Almost all WWTPs experience fluctuations in influent flows and loading due to diurnal, seasonal, or event-related (e.g., storms) variability. While measures such as flow equalization can be taken to reduce the overall magnitude of such variability, WWTP effluent quality, and hence AWTF influent quality, also experiences these fluctuations. Additionally, operational changes in the WWTP, such as periodic use of as-needed bleach or coagulant addition, or at the AWTF, such as backwashing, membrane replacement, membrane cleaning, or equipment startup/shutdown, can result in fluctuations in water quality. The challenge of differentiating occurrence of true chemical peaks (due to abnormal events such as intentional or unintentional illicit discharge) is to distinguish these disturbances from the normal variations seen in the facility.

The use of online TOC analyzers has been widely accepted as the preferred method of RO performance monitoring to ensure membrane and process integrity. The efficacy of using these analyzers for detecting chemical peaks is discussed in greater detail in Chapter 6, but for the purposes of this analysis, TOC analyzers are assumed to sufficiently measure the occurrence of the broad spectrum of organic compounds previously discussed.

In order for a disturbance to be classified as a chemical peak, the measurement (i.e., online TOC) must deviate from the variable baseline (peak height) and be present for a significant length of time (peak width). Peak width and height will be different between facilities as well as between disturbance events, and so minimum requirement guidelines must be established.

3.1 Defining the Baseline

The concentration and variability of TOC in RO feed waters will differ between AWTFs based on the source water, treatment process utilized, and operational practices. RO permeate will also experience fluctuations based on operation of the RO trains. Changes in permeate flow, flux, and startup/shutdown of RO trains can result in short-term variations in permeate TOC. The TOC baseline must therefore be determined for each facility. Baseline monitoring can be conducted during pilot testing and/or during the first month(s) of startup.

Baseline monitoring should be utilized to determine not only the range of background TOC concentrations during normal operating conditions, but also the rate of change of TOC concentrations. Piloting and startup are opportunities to document changes in RO feed and permeate TOC concentrations during or after operational events such as backwashing, chemical cleaning, and startup/shutdown of RO trains. The TOC responses to these events should be documented so that operators/staff can both predict TOC fluctuations prior to an operational event as well as identify the effects of the operations on TOC when analyzing TOC data in real time or in retrospect.

3.2 Chemical Peak Width

Chemical peaks within the scope of this project refer specifically to intentional or unintentional illicit discharges into the sewershed. The resulting chemical peak will therefore have a finite length before conditions return to normal operations. Transport within the sewershed is not expected to be true plug flow, and dispersion/mixing is expected prior to reaching the WWTP. The size of the discharge and the location within the sewershed will affect how much dispersion/mixing occurs. After reaching the WWTP, additional dispersion occurs within the facility, as the unit processes similarly do not operate as true plug flow systems. Mixing within basins, as well as return processes such as internal recycle and return activated sludge transport, will also result in a “tailing” of the peak. The combination of dispersion through the sewershed and the WWTP will result in a minimum peak length from several hours to several days long (Laurent et al. 2014, Potier et al. 2005, Burrows et al. 1999), even if the illicit discharge itself was short-lived or “instantaneous”.

If an illicit discharge occurs within the collection system, the chemical peak observed in the TOC data will not result in a near-instantaneous increase in TOC from baseline conditions. Rather, dispersion in both the sewershed and the WWTP will result in the peak having a “leading edge” (i.e., a slope) characterized by an increase in TOC that is more rapid than increases observed during normal diurnal variations, but can take multiple hours to reach a maximum peak height (Laurent et al. 2014, Potier et al. 2005, Burrows et al. 1999). The rate of increase in TOC is therefore an essential consideration when attempting to classify chemical peaks.

The definition of peak width on the scale of hours to days is important to reduce the number of “false positives” or incorrectly identified events that could result in unnecessary operational responses. Data from a single measurement of an analyzer cannot be relied upon to make operational decisions, as instrument drift or interferences such as bubbles in the sample line or electrical surges can result in errant signals. Multiple consecutive data points, with a minimum of three, should therefore be used to designate an excursion when attempting to identify the start of a potential peak.

Under the Surface Water Treatment Rule, the minimum required sampling interval for an analysis to be considered continuous is fifteen minutes. This sample period allows for travel time of a sample from the process to the analyzer, analyzer reaction time, and time to display or transmit results. The collection of three data points with this minimum sample interval would take a total of thirty minutes from the first measurement above the baseline to detect a chemical peak. Given that chemical peaks are expected to last on the order of hours to days, a fifteen minute minimum sampling interval is therefore sufficient to detect a chemical peak without the risk of the peak passing through the treatment system undetected. It is therefore not recommended that the minimum sample interval of fifteen minutes be decreased to a shorter time, as this is not necessary to ensure chemical peak detection. In addition to peak width, or duration, additional criteria such as peak height need also to be met, in order to distinguish chemical peak from variability in the baseline.

3.3 Chemical Peak Height

As discussed above, variations in AWTF feed water quality complicates the determination of a chemical peak in the system. Average TOC and diurnal/seasonal variability in RO feed and permeate will vary between facilities based on influent water quality, treatment processes utilized, and operational practices. The following discussion represents guidelines for facilities, which will need to assess their individual systems prior to determining a unique control strategy.

For the purposes of this discussion, the TOC threshold above which may indicate a deviation from baseline conditions and could signify the presence of a chemical peak will be referred to as the “baseline threshold.” The actions taken by the AWTF when the baseline threshold is exceeded may vary between facilities, and development of potential response actions for a given TOC concentration is outside the scope of the present evaluation. TOC readings that exceed the baseline threshold for the minimum three consecutive measurements will be referred to as “excursions,” as the deviation from normal conditions does not immediately imply the presence of a chemical peak, but rather requires further investigation before classification as a chemical peak.

To be classified as a chemical peak, TOC concentrations must deviate from normal operating conditions. Numerous statistical methods can be utilized to classify the distribution of TOC concentrations measured by the online analyzers during normal operating conditions. It is important to note that without filtering or otherwise modifying the dataset, the measured concentrations will include outliers which will affect calculated metrics. For example, if regular (repeated) instrument errors lead to enough outliers that are significantly higher than normal operating conditions, the calculated average and standard deviations of the dataset could be skewed. A robust, conservative metric must therefore be utilized to characterize the dataset as accurately as possible.

When identifying potential outliers in large datasets, the interquartile range (IQR) is commonly used. The IQR is defined as the difference between the 75th percentile of the dataset (quartile 3; Q3) and the 25th percentile of the dataset (quartile 1; Q1). The IQR therefore represents the middle 50% of the data, and is only affected by outliers if the outliers are present at a rate of 25% above or below the IQR, at which point, there is a serious issue with the instruments being utilized. To identify potential outliers, the baseline threshold is set at 1.5 times the IQR above the 75th percentile of the dataset (Tukey 1977, Hoaglin et al. 1986), or:

$$\text{Baseline Threshold} = Q3 + 1.5 * IQR \qquad \text{(Equation 3-1)}$$

where: Q3 = third quartile
IQR = interquartile range (Q3-Q1)

Examples using real data are provided in the next section below. As discussed above, this baseline threshold will be utilized as the minimum TOC concentration required for an event to be classified as an excursion from baseline conditions, and upon verification of additional characteristics (i.e., width and rate of increase) the excursion could be classified as a chemical peak. The baseline threshold can therefore be considered the minimum peak height. Again, excursions above the baseline threshold do not automatically result in the classification as a chemical peak and must be further examined before operational actions occur.

Pilot studies and facility startup can be utilized to provide the range of normal operating conditions and to define the baseline threshold above which chemical peaks may be present. As the facility continues to operate, however, aging of membranes, operational changes, or influent water quality changes may result in slow shifts of the baseline conditions. It is therefore recommended that the baseline threshold be recalculated annually, with quarterly review of the applicability of the baseline threshold value.

3.4 Chemical Peak Detection

In order to be classified as a chemical peak due to an illicit discharge, the following criteria must be met:

1. Peak height must exceed a threshold above the normal baseline variation in RO permeate TOC. This baseline threshold can be set as the 75th percentile of annual data (quartile 3) plus 1.5 times the IQR (quartile 3 minus quartile 1)
2. Peaks must exceed the baseline threshold for at least three consecutive measurements with the online TOC analyzer to qualify as an excursion. AWTFs operating at high sampling frequencies may choose to increase the number of required points to provide adequate response time.
3. Peaks must last from several hours to days

For the real time detection of peaks, elimination of outliers is crucial to limiting the number of false peak identifications. The use of redundant TOC analyzers can flag potential outliers, as readings that do not closely match can be investigated; however, redundant analyzers is not a catch-all solution. If the readings from two analyzers are different, it is impossible to know which analyzer is correct without verification from a grab sample or an additional analyzer. Dual analyzers also result in increased operations and maintenance time and cost.

For a single analyzer, a minimum of three consecutive measurements above the baseline threshold must be made to have confidence that an excursion, which may be a chemical peak, is occurring, and reduce the likelihood that it was instrument error causing the elevated reading. For the minimum required fifteen-minute sample interval, this would result in the samples being collected over a thirty-minute time period. For facilities utilizing more frequent sampling, a greater number of consecutive measurements above the peak height threshold could be utilized to allow for a similar operator response time.

Though TOC online monitoring is generally done on both the RO feed and RO permeate streams (as related to evaluation of RO integrity and pathogen reduction credits), chemical peak detection in potable reuse facilities is expected to focus on the RO permeate. This is because TOC measurements from the RO feed cannot reliably be used to classify the presence of a chemical peak, since the chemical peak may be a small portion of the TOC in the RO feed, and thus may go unnoticed. TOC rejection across the membranes, however, could be an indicator of a chemical peak, as the increased RO permeate TOC due to low chemical rejection could significantly impact the calculated TOC rejection. More research into the use of TOC rejection as a control metric is needed before this strategy can be recommended.

To vet the proposed definition of a chemical peak, real data from 2013-2019 from the OCWD GWRS RO facility was analyzed. Baseline thresholds were calculated for each calendar year of data. It is worth noting that in the six years of data collected, the TOC concentrations were below the baseline threshold >99.5% of the time. Therefore, regular monitoring of the RO permeate is an ineffective method to identify chemical peaks. However, obtaining grab samples once a chemical peak has been confirmed by TOC analyzers is desirable to identify the chemical(s) causing the peak and informing the source control program in an effort to eliminate the identified chemical(s) from the sewershed (see Section 2.2.6).

Online TOC data from 2018 for the two RO permeate TOC analyzers (duplicate analyzers), each programmed to collect a reading every two minutes, was pooled together and the baseline threshold calculated with Equation 3-1 as 0.080 mg/L. A subset of the data from October 2018 with RO permeate analyzers TOC1 (gray) and TOC2 (blue) are shown below in Figure 3-1.

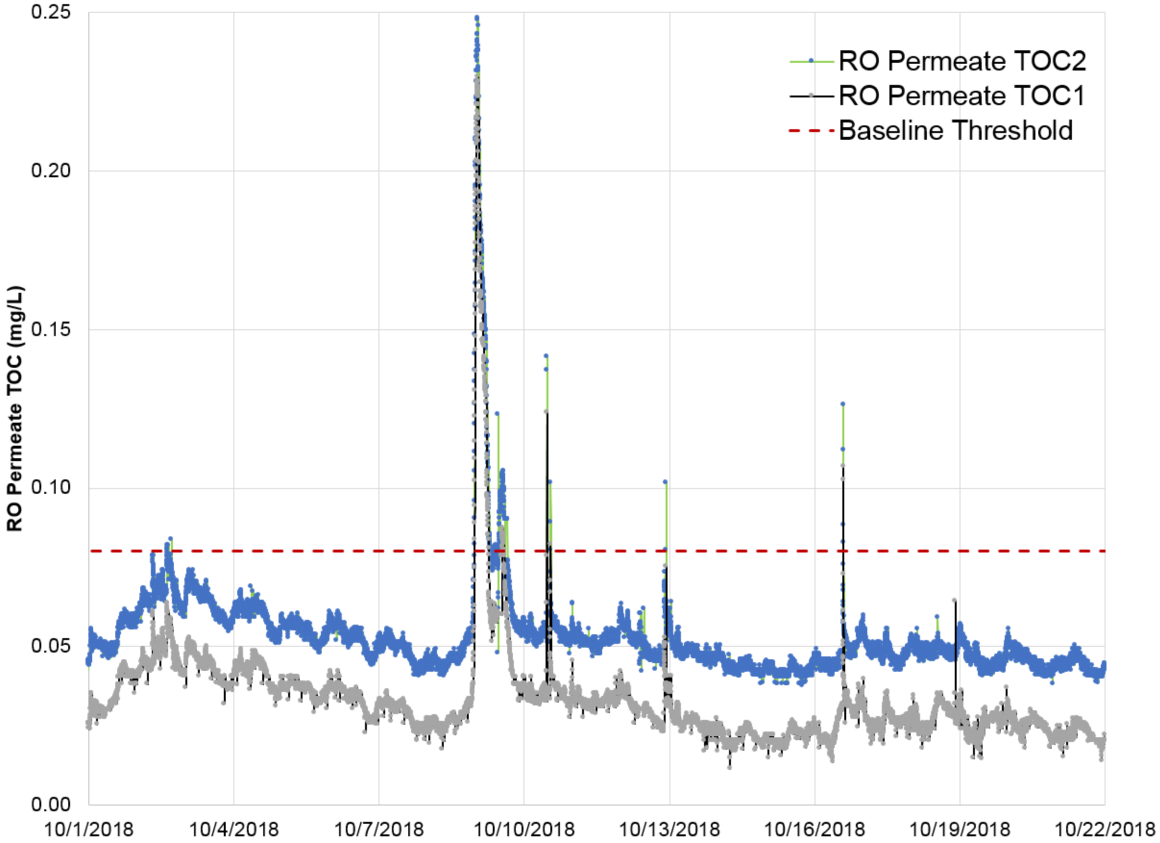

Figure 3-1. RO Permeate Data from Analyzers TOC1 and TOC2.
Dashed red line indicates calculated baseline threshold of 0.08 mg/L.

RO permeate analyzer TOC1 was consistently offset from TOC2 by approximately -0.02 mg/L. Due to the lower concentration of TOC1, all analysis below will be conducted on TOC2, as the TOC concentrations are closer to the baseline threshold (worst case scenario). Figure 3-2 shows the potential chemical peaks, identified as exceedance events above the baseline threshold, that will be investigated.

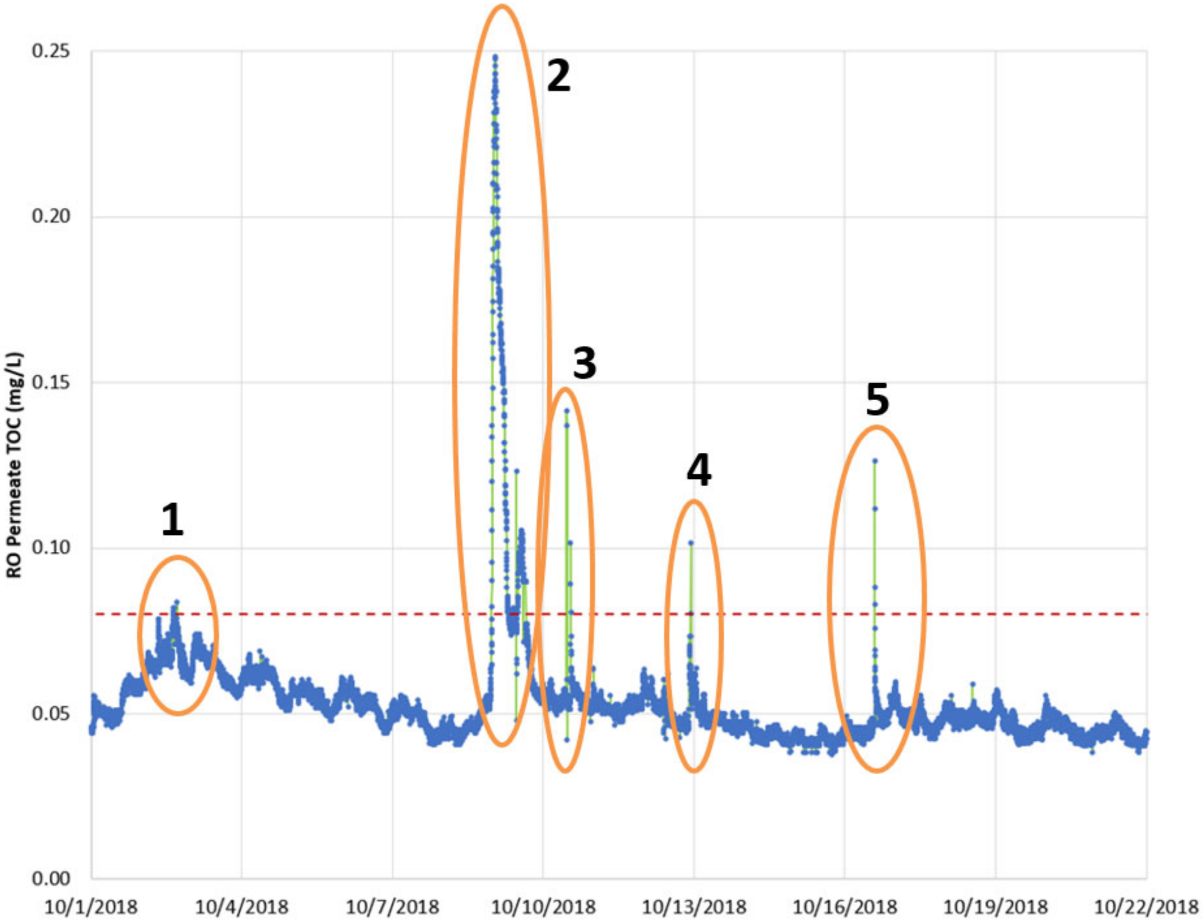

Figure 3-2. Potential Chemical Peaks in RO Permeate TOC2.

Exceedance Events 1-5 will be addressed in Figures 3-3 through 3-7. Red dashed line indicates baseline threshold.

Figure 3-3. RO Permeate TOC Exceedance Event 1 from Figure 3-2.
Red dashed line indicates baseline threshold.

The event shown in Figure 3-3 exceeded the baseline threshold for three consecutive data points, making the event an excursion from baseline conditions. However, the three consecutive points were all decreasing, suggesting that these points were not the start of a chemical peak. Subsequent data were below the baseline threshold, with two additional non-consecutive exceedance points over the next few hours. The lack of a sustained, rapid increase in TOC, the limited points above the baseline threshold, and the short duration all lead to a determination that this excursion was not a chemical peak.

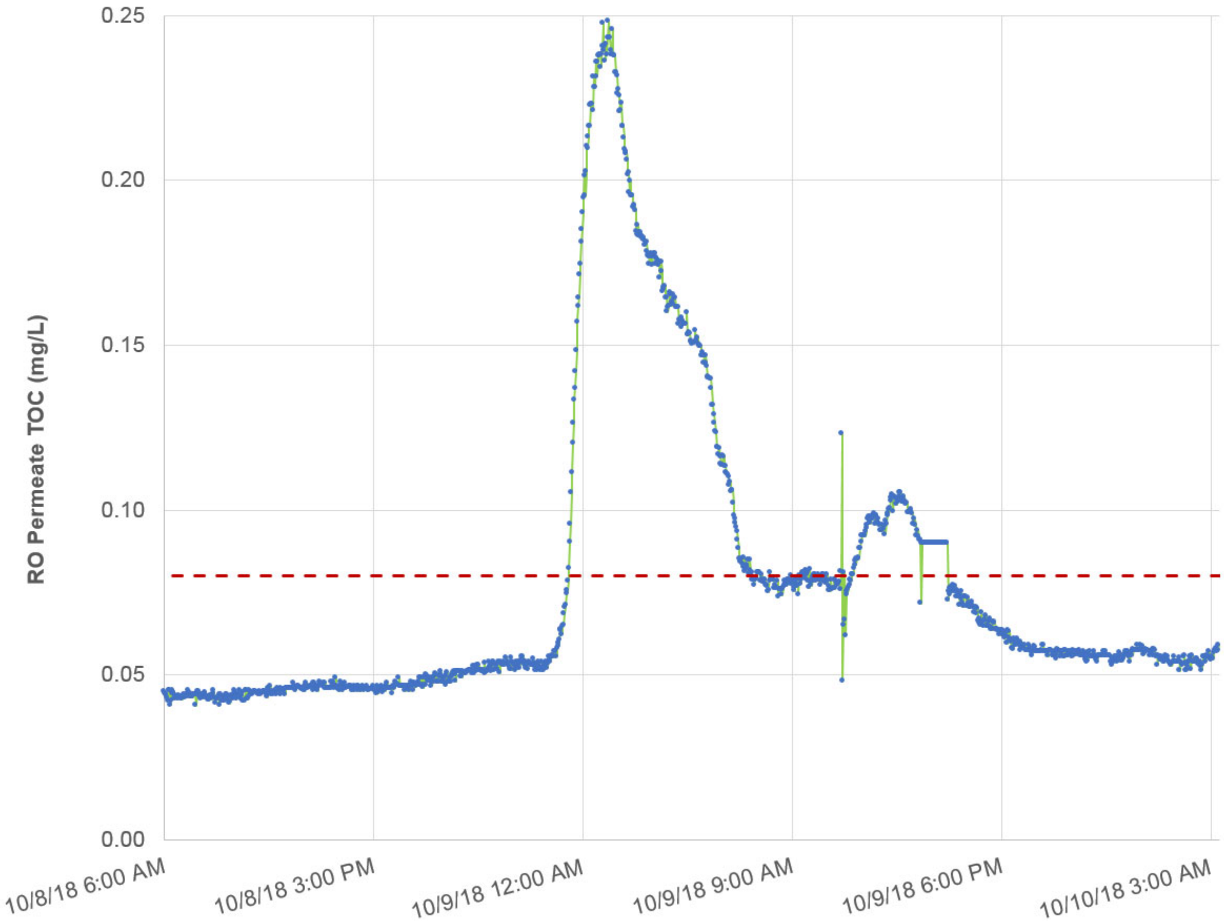

Figure 3-4. RO Permeate TOC Exceedance Event 2 from Figure 3-2.
Red dashed line indicates baseline threshold.

The event shown in Figure 3-4 exceeded the baseline threshold for approximately nine hours, followed by a secondary shoulder that exceeded the baseline threshold for approximately four hours, and returned to baseline conditions after approximately 20 hours. The event qualifies as an excursion from baseline conditions as more than three consecutive measurements were above the baseline threshold. At the beginning of the excursion, there was a steep increase in TOC concentration, increasing at a rate faster than normal diurnal variations, indicative of the start of a peak event. By the time that the first three data points exceeded the baseline threshold, concentrations had been rapidly increasing for approximately ninety minutes. The length of the excursion meets the proposed definition of peak length. Finally, the height of the peak, which meets the minimum peak height requirement since the peak exceeds the baseline threshold, reached approximately three times the baseline threshold concentration, and the tailed shape of the excursion make this a likely chemical peak due to an illicit discharge.

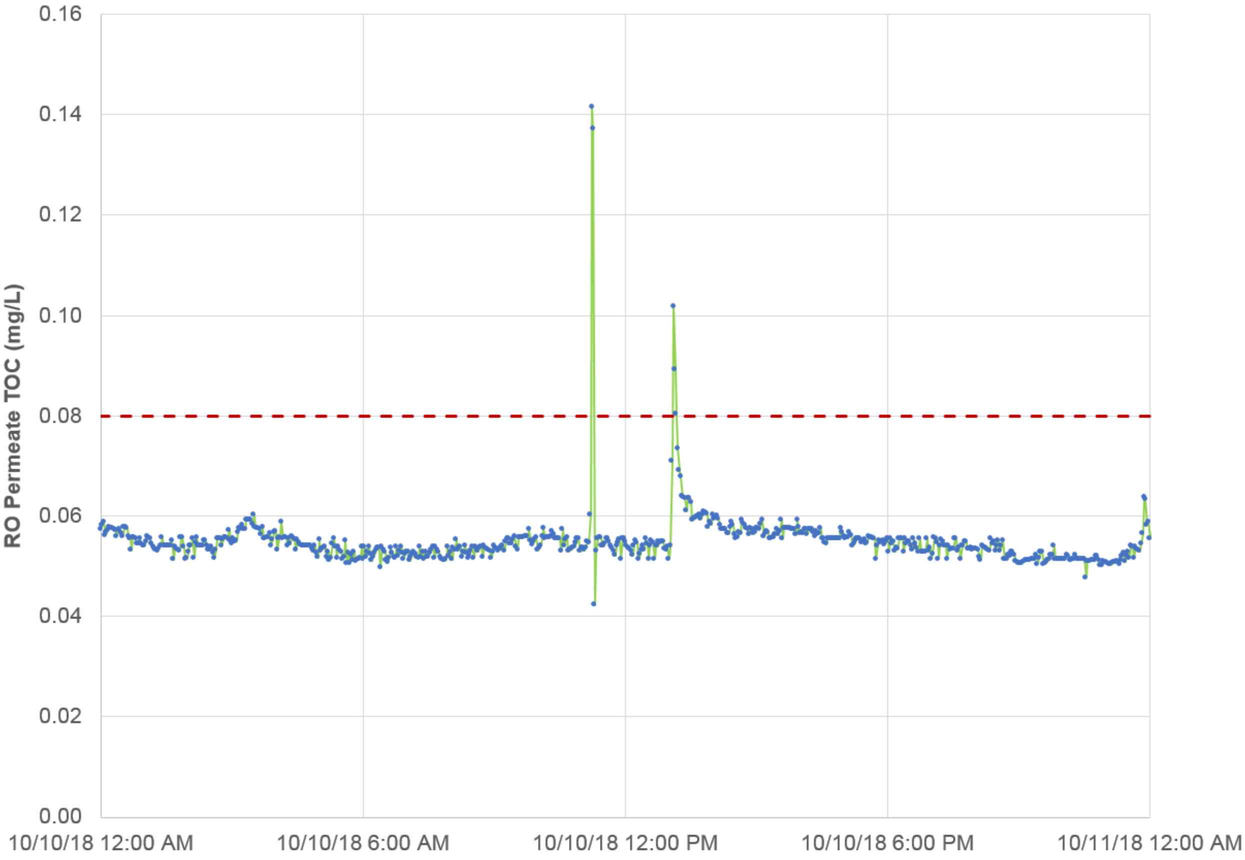

Figure 3-5. RO Permeate TOC Exceedance Event 3 from Figure 3-2.
Red dashed line indicates baseline threshold.

The exceedance shown in Figure 3-5 has two events that exceed the baseline threshold. The first, occurring at approximately 11:00 AM on 10/10/18, has only two data points measured above the baseline threshold before returning to baseline conditions. This event does not qualify as an excursion as it does not meet the minimum criteria of peak width and is likely the result of an analytical error.

The second event at approximately 1:00 PM on 10/10/18 has three consecutive data points measured above the baseline threshold for approximately 4 minutes, qualifying as an excursion. These points, however, are all decreasing, reducing the likelihood that a peak event is starting. Importantly, the extremely rapid start and short duration of the excursion make it highly unlikely to be a chemical peak, per the previous discussion that an illicit discharge is very likely to result in peaks that last hours to days due to dispersion and lack of true plug flow in the collection system, WWTP, and AWTF. However, this excursion is likely not instrument error, as the tail of the peak is well defined. The excursion is likely caused by an operational event in the AWTF, such as a backwash or startup of a RO train, and is not the result of a chemical peak due to an illicit discharge.

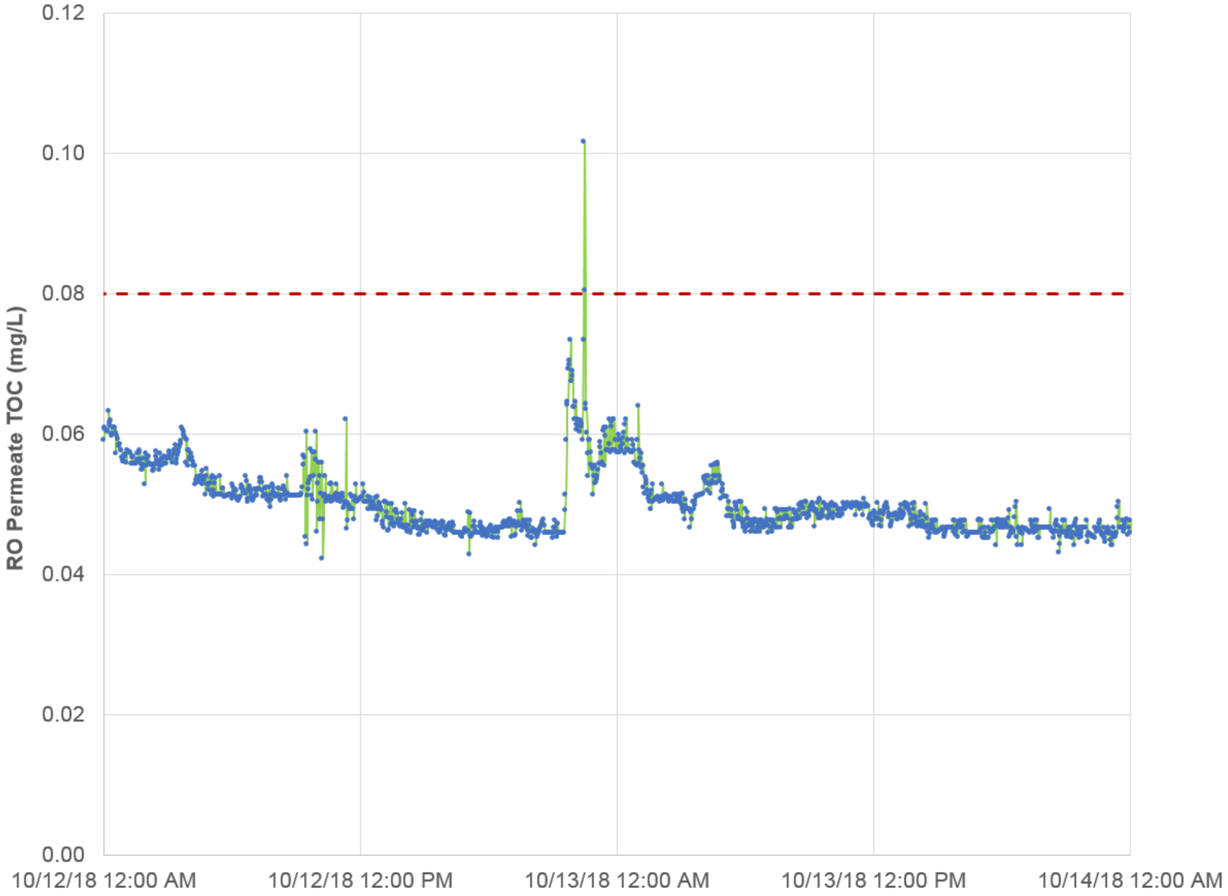

Figure 3-6. RO Permeate TOC Exceedance Event 4 from Figure 3-2.
Red dashed line indicates baseline threshold.

The event shown in Figure 3-6 has only two consecutive data points measured above the baseline threshold, and therefore does not meet the minimum criteria for classification as an excursion. This exceedance is likely due to instrument error but may have occurred during an operational event.

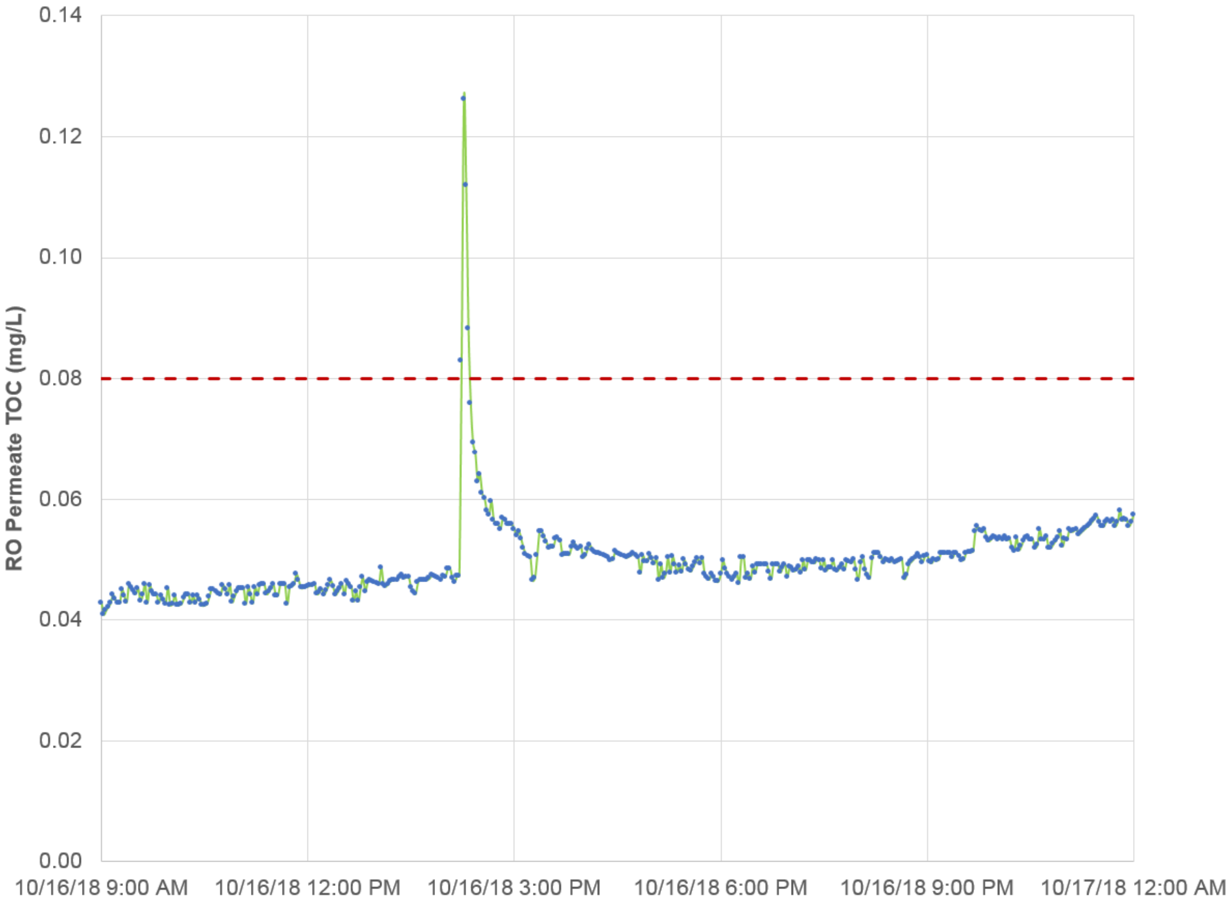

Figure 3-7. RO Permeate TOC Exceedance Event 5 from Figure 3-2.
Red dashed line indicates baseline threshold.

The exceedance event shown in Figure 3-7 has four consecutive data points measured above the baseline threshold, qualifying as an excursion. The first two points have increasing values, followed by a decrease over the next two points. The rapid increase in TOC concentration followed by the exponential decrease to baseline conditions again indicates an event likely linked to an operational change rather than a chemical peak due to an illicit discharge.

In summary, of the five exceedance events above the baseline threshold noted in Figure 3-2, only Event 2 is likely indicative of a chemical peak due to an illicit discharge. Of the remaining events, a brief exceedance in Event 3 and Event 4 are likely analytical errors, the excursions in Event 3 and Event 5 are likely due to operational events, and the excursion in Event 1 is indicative of normal variation at the upper end of the baseline condition.

After analyzing the exceedance events shown above, OCWD staff provided operational information regarding the events. Exceedance Event 3 was verified as occurring directly after the startup of a RO train. Exceedance Event 5 was also verified as the result of startup of a RO train after membrane replacement. These short-term spikes, commonly seen in the startup of RO trains, represent an increase in background TOC with similar composition as during normal operation, and do not signify any significant change in permeate water quality that require additional treatment or mitigation steps.

CHAPTER 4

Case Studies

Three utilities (City of San Diego [City], Singapore Public Utilities Board [PUB], and Orange County Water District [OCWD]) were surveyed to share their experiences of detected chemical peaks as well as response protocols during such events. This chapter also evaluates the impacts of illicit discharges for different sewersheds and chemical volumes and identifies available options for chemical peak "averaging." In addition, implications of chemical peaks on different DPR scenarios are discussed.

4.1 Source Control and Source Water Monitoring for DPR

Municipal wastewater contains discharges from residential, commercial, and industrial sources as well as stormwater infiltration/inflow. The diversity of these sources provides variability in the constituents and mass loads that are inherently discharged into the sewershed. This variability makes it difficult to predict possible impacts to wastewater treatment plants, especially in events of illicit discharge. Source control programs are implemented with the goal of reducing (or eliminating) the discharge of constituents that are difficult to manage from a treatment and environmental standpoint (Tchobanoglous et al. 2015).

Specifically for potable reuse, it is important to recognize the shift of historically separating sewershed from watershed to a paradigm where the sewershed is seen as a resource to augment potable water supplies. As such, a key factor in achieving reliable potable reuse is to recognize that a source control program is critical in creating a safe water supply that does not focus solely on wastewater discharge compliance. Another key aspect to achieve potable reuse reliability is source monitoring. To complement or enhance a conventional source control program for potable reuse, online monitoring of the sewershed may be considered to provide early warning to the FAT facility and also help identify the location of the chemical discharges that may impact the source quality. The more that industrial flows contribute to the overall wastewater load and flow to be treated for reuse, the more likely it is that an agency would benefit from incorporating a sewershed monitoring system[1]. Due to this concern, international facilities, such as the DPR facility in Windhoek, Namibia, and some NEWater facilities in Singapore, isolate the industrial flows and do not utilize them for potable reuse applications. Unlike those countries, the United States has a Federal pretreatment program that has been created as part of the 1972 Clean Water Act and industrial flow is commonly commingled with the municipal flow received at wastewater treatment facilities. Information on the source control programs from the case study utilities is summarized below and more detailed information is provided in referenced materials.

4.1.1 Overview and Purpose of the National Pretreatment Program

The National Pretreatment Program was established as part of the 1972 Clean Water Act (CWA) to control and regulate the release of pollutants from commercial and industrial wastewater dischargers to publicly owned treatment works (POTWs) (USEPA 2011). The objectives of the program are to:

1. prevent the introduction of pollutants that will interfere with the operation of a WWTP, POTW, "treatment works" or similar,

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[1] In some cases, to minimize the impact from large industrial dischargers, it may be appropriate to consider diverting highly industrialized discharges to alternative treatment facilities (Tchobanoglous et al. 2015).

2. prevent the introduction of pollutants that will pass through the treatment works or otherwise be incompatible with it, and
3. improve opportunities to recycle and reclaim municipal and industrial wastewaters.

Per the Code of Federal Regulations (40 CFR 403.8), any POTW that discharges to surface waters under a National Pollutant Discharge Elimination System (NPDES) permit "with a design flow greater than 5 million gallons per day (MGD) and receiving […] pollutants which pass through or interfere with the operation of the POTW" are required to establish a Pretreatment (USEPA 2011)[2]. A POTW subject to the National Pretreatment Program must enforce both general and specific prohibitions.

Specific discharge prohibitions that must be enforced include:

1. Pollutants that may create a fire or explosion hazard in the sewer system or at the POTW
2. Corrosive pollutants, including any discharge with a pH of less than 5
3. Solid or viscous pollutants in sufficient amounts that will cause obstruction or blockage of flow
4. Any pollutants discharged in sufficient quantity to interfere with the operation of the POTW
5. Heat in such quantities that the temperature at the POTW treatment plant exceeds 104°F or is hot enough to interfere with biological treatment processes
6. Petroleum oil, non-biodegradable cutting oil, or other products of mineral oil origin in amounts sufficient to cause interference or pass-through
7. Pollutants that result in the presence of toxic gases, vapors, or fumes at the POTW in sufficient amounts to cause acute worker health and safety problems
8. Any trucked or hauled pollutants, except at discharge points designated by the POTW

In addition, a POTW subject to the National Pretreatment Program must maintain a list of all industrial users that discharge to the sewershed and develop local limits to regulate the discharge of pollutants of concern from industrial users[3]. The procedures to ensure compliance with pretreatment standards are based on the following three elements:

1. Receiving and analyzing self-monitoring reports and other notices submitted by industrial users
2. Random sampling and analysis of effluent from industrial users
3. Conducting surveillance activities to identify compliance or noncompliance that is independent from information supplied by industrial users

Although the National Pretreatment Program provides a strong foundation in terms of protecting a POTW from industrial user discharges, the program was not originally envisioned to support and protect potable reuse projects.

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[2] The EPA may require that a POTW with a design flow of 5 MGD or less develop a POTW Pretreatment Program if it is found that the nature or volume of the industrial influent, treatment process upsets, violations of POTW effluent limitations, contamination of municipal sludge, or other circumstances (such as the practice of potable reuse) warrant in order to prevent interference with the POTW or pass through.

[3] The EPA does not regulate all chemicals, including those that may still be unknown. As such, research is needed to develop more comprehensive methods to identify unknown compounds that may be of concern. Such compounds may be discharged by research facilities, commercial facilities and/or illegal discharges.

4.1.2 Source Control Programs of Case Study Utilities

The following subsections provide a non-exhaustive description of the case study utility source control programs. References are provided for additional review. Table 4-1 provides key metrics summarizing the three utilities.

Table 4-1. Source Control Program Key Metrics for Case Study Utilities.

Utility	Orange County Sanitation District	City of San Diego	Public Utilities Board Singapore
Year source control program was established	Regulations first adopted in 1954. Pretreatment program recognized by EPA in 1984.	Pretreatment program recognized by EPA in 1982.	Regulations first adopted in 1999. Since 2004, PUB has enhanced its source control program to what it is today.
Range of flows	183 – 207 MGD	About 150 MGD	353 – 357 MGD
Number of industrial dischargers	555 active permits as of 2018-19 fiscal year	1,300 active permits as of December 2017	Presently up to 5,000 industrial premises under surveillance
Area of sewershed	479 square miles	450 square miles	270 square miles
Length of collection system	389 miles	2,900 miles	2,237 miles

4.1.2.1 Orange County Sanitation District

The Groundwater Replenishment System (GWRS), a joint project of OCWD and Orange County Sanitation District (OC San), is currently the world's largest advanced water purification system for potable reuse. Source water to the GWRS is secondary-treated wastewater from the OC San Plant No. 1 – both facilities are located in Fountain Valley, California. OC San's service area is comprised of approximately 87% raw wastewater from residential sources and 13% from commercial and industrial sources (OC San 2015). Since 1984, OC San maintains an EPA approved pretreatment program which has been successful at reducing the average daily pounds of metals entering their system. OC San's pretreatment program consists of the following components:

1. Control mechanisms: OC San uses two control mechanisms to regulate industries (Industrial Waste Discharge Permits and Wastewater Discharge Regulations Ordinance). Permits and the ordinance define the regulations industries must follow.
2. Monitoring program: OC San routinely samples industrial wastewater dischargers and inspects facilities. The program can require industrial dischargers to perform self-monitoring of their discharges and submit certified laboratory data.
3. Compliance screening: OC San performs compliance screening to locate violators. The violators are identified by comparing sample results against permit limits. Notices of violation are issued and sent to the violating discharger. Violations are also issued for late submittal of reports.
4. Implementation of enforcement actions: violations are reviewed to determine if OC San should issue a warning, fine, or pursue criminal charges.

During the 2017/18 fiscal year, OC San administered more than 550 active permits:

1. 336 Class I permits
2. 21 Class II permits
3. 41 Waste Hauler permits
4. 60 Special Purpose permits
5. 21 Urban Runoff permits
6. 39 Fat, Oil, and Grease permits
7. 23 zero discharge certifications

OC San has also developed several innovative features to their source control program to enhance reliability, including:

1. Implementation of mass and concentration limits: OC San has implemented mass limits in addition to concentration limits to control and reduce toxic materials discharged to the sewer.
2. Pollution prevention program: OC San requires industries to provide waste management plans to conserve water and to have pollution prevention techniques.
3. Technical assistance center: OC San periodically conducts workshops and publishes educational brochures related to permitting, sewer connections, compliance, and pollution prevention.
4. Waste hauler program: regulates the type of waste that can be hauled to OC San Plant No. 1.
5. Non-industrial source control program: OC San promotes and implements a variety of waste management strategies and practices to reduce or eliminate the generation of waste at the source.

4.1.2.2 City of San Diego

The City of San Diego's (the City) source control program is administered by the City's Industrial Wastewater Control Program. The program applies and enforces federal pretreatment regulations for the entire Metropolitan Wastewater/Sewage System. As of 2017, the service area for Point Loma WWTP (the City's main WWTP) is comprised of approximately 94% raw wastewater from non-industrial sources and 6% industrial sources (City of San Diego 2017). The North City Water Reclamation Plant, which will serve effluent to the future North City Pure Water Facility, will have an industrial flow contribution of 2% after the facilities' sewershed is expanded to 52 MGD (City of San Diego 2019). San Diego has a history of operating an enhanced Source Control Program with a high degree of success. Effective implementation of this enhanced control program is required in order to qualify for and maintain the modified NPDES permit for the Point Loma Wastewater Treatment Plant (PLWTP) that obviates the need for secondary treatment at that location. It is noteworthy that the effectiveness and diligent implementation of this enhanced program has allowed the PLWTP to operate with a modified permit for over 20 years. More details about the City's Source Control Program are available in the City's Annual Pretreatment Report (City of San Diego 2017).

The City's source control program applies and enforces federal pretreatment regulations set forth by the EPA and pursuant to 40 CFR 403 and the Clean Water Act. The program serves to:

1. Protect and improve receiving water quality.
2. Prevent the discharge of toxic and potentially harmful pollutants in concentrations that would interfere with treatment plant operations or pass through the plant to the receiving waters.
3. Protect system personnel and plant facilities by limiting discharges of potentially hazardous, harmful, or incompatible pollutants.
4. Prevent contamination of treatment plant sludge to maximize beneficial reuse options for biosolids.
5. Protect the quality of recycled water.

As of December 31, 2018, the City of San Diego Source Control was administering more than 1,289 permits:

1. 36 Class I permits
2. 297 Class II permits
3. 54 Class III permits
4. 143 Trucked Waste permits
5. 32 Groundwater Discharge permits
6. 759 Best Management Practice Discharge Authorization permits

In 2018, the City performed 378 inspections, 1,456 unannounced sampling visits. A total of 12,294 pollutants measurements were performed and 385 Notices of Violation were issued to industries that exceeded discharge limits or failed to comply with permit conditions. Table 4-2 provides metrics of these source control measures from 2009 to 2018.

Table 4-2. City of San Diego Source Control Key Metrics from 2009 to 2018.

Year	Number of Inspections	Unannounced Sampling Visits	Pollutants Measured	Notices of Violation
2009	917	2,063	17,778	292
2010	719	2,052	15,786	275
2011	697	2,392	18,773	288
2012	794	1,971	17,343	242
2013	611	2,241	18,543	240
2014	545	2,050	18,538	203
2015	596	1,597	16,849	204
2016	495	1,671	9,886	247
2017	343	1,513	12,294	315
2018	378	1,456	16,253	385

Since federal approval of the City's Source Control Program in 1982, the mass of heavy metals entering the City's sewershed collection decreased by more than 67%[4]. In addition, the City's sludge qualifies as "exceptionally clean" under criteria set forth in the Code of Federal Regulations, which attests the effectiveness of the City's Source Control Program and opportunities for beneficial reuse of sludge.

The City's federally approved source control program has been able to reduce the load of heavy metals and enforce discharge violations through aggressive measures, such as:

1. an industrial wastewater discharge permit system to establish industrial discharge limits and requirements;
2. periodic facility inspections and unannounced sampling;
3. effective enforcement procedures to deter violations and bring noncompliant dischargers back into compliance with discharge standards and requirements, and;
4. industrial user guidance and permit conditions designed to encourage pollution prevention and waste minimization.

4.1.2.3 Public Utilities Board (PUB) of Singapore

PUB's source control program consists of multiple components that include regulation of industries discharging to the network and an extensive sewershed monitoring program. Pursuant to the Sewerage and Drainage Act, a trade premise (i.e., industrial discharger) must obtain written approval from the PUB prior to discharging to the public sewer (Government of Singapore 1999). This requires the trade premise to declare the types of chemical uses and may require the installation of pretreatment and/or appropriate monitoring equipment as designated in the Sewerage and Drainage Act. An approved trade premise must ensure that its discharge is in compliance with the discharge requirements. If the trade premise is categorized as a high-risk discharger, audits and checks of effluent samples are conducted on a monthly to quarterly basis. Low risk dischargers are surveilled biannually or annually.

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[4] Data from the pretreatment reports shows that there has been a steady decline in industrial pollutants discharged to the Point Loma Wastewater Treatment Plant (PLWTP) over the past 30 years. Enforcement of Pretreatment Standards and implementation of Source Control Programs have effectively reduced pollutant loadings at the plant headworks, ensuring that there are no incidents of pass-through or interference attributed to industrial discharges at the Point Loma facility. Some of the reduction is attributed to the diversion of wastestreams to the South Bay and North City Water Reclamation Plants.

PUB's source control program was developed to manage wastewater discharge quality to support water reclamation. To achieve this goal, PUB uses a four-pronged approach:

1. Stake holder engagement and education to create awareness among trade premises
    a. Regular dialogues with associations
    b. Press releases to publicize the importance of sewer protection and consequences for breaching requirements
    c. Clear labeling of discharge prohibitions on chemical products
2. Develop a robust enforcement regime to deter and penalize offenders
    a. Increase inspection frequency for high risk dischargers
    b. Revoke discharge certificate/approval, if necessary
3. Effective monitoring measures to prevent and deter at the source
    a. Close monitoring using volatile organic chemical (VOC) and auto-sampler units
    b. Security-sealing of manholes
    c. Audit operations
4. Empowering staff and online monitoring enhancements
5. Offer training and courses
6. Closing knowledge gaps through research and development

PUB currently prohibits the discharge of organic compounds classified as industrial waste as specified in the Environmental Public Health (Toxic Industrial Waste) Regulations, petroleum spirits and other flammable substances. Furthermore, under the current Sewerage and Drainage Act, PUB specifically prohibits the discharge of 30 organic compounds to the public sewer. A list of the prohibited compounds is provided in Table 4-3. The Government of Singapore developed the Sewerage and Drainage act in order to protect water that is eventually treated to potable quality (Soon et al. 2009).

Table 4-3. List of Prohibited Organic Compounds That Cannot Be Discharged to PUB Public Sewer.

List of Prohibited Organic Compounds (PUB)		
1,2,4-Trimethylbenzene	Furan	Octane
1,1,1-Trichloroethane	Heptane	Polybrominated diphenyl ether
1,1,2-Trichloroethane	Hexane	Styrene
Benzene	Isobutanol	Tetra-chloromethane
Decane	Isopropyl ether	Tetra-chloroethylene
Diethyl ether	Methyl ethyl ketone	THF (Tetrahydrofuran)
Dimethyl sulphide	Methyl isobutyl ketone	Toluene
Dimethyl sulphoxide	Methyl tert-butyl-ether	Trichloroethylene
DMF (N,N-Dimethylformamide)	Methylene chloride	Turpentine
Ethylbenzene	Nonane	Xylene (o,m,p)

4.1.3 Development of an Enhanced Source Control Program for Direct Potable Reuse

Specific to DPR, it is important to understand the impact of chemicals that could adversely impact drinking water quality and the potential sources of toxic compounds that may enter the sewershed, particularly from industrial dischargers. The following are measures that can be incorporated into DPR enhanced source control programs (adapted from Tchobanoglous et al. 2015):

1. Regulatory authority
    a. Ensure that the source control program has legal authority to develop and implement source control measures. This should include authority for oversight and inspection, as well as review of new connections to the collection system.

2. Monitoring and assessment of commercial and industrial discharges to the wastewater collection system within the service area
    a. Influent and effluent of wastewater treatment plant (WWTP) are routinely monitored for regulated constituents and other constituents that may be discharged into the collection system service area.
3. Source investigation of chemical and other constituent sources
    a. Develop and maintain a frequently updated, comprehensive inventory of industries and businesses that use or generate chemicals that are of concern.
4. Maintenance of current inventory of chemical constituents
    a. Develop and maintain a database of the chemicals stored and inventory volume used annually by industrial and commercial producers in the service area.
5. Preparation of public outreach and participation programs
    a. Provide public outreach information on DPR to industries,
    b. Develop a program that encourages commercial and industrial dischargers to be partners in protecting the sewershed,
    c. Develop school educational programs that address source control issues related to potable reuse.
6. Preparation of a response plan for water quality deviations
    a. Interagency collaboration between WWTP and advanced water purification facility (AWPF) to ensure successful and prompt responsiveness when water quality excursions occur.

Though a DPR-tailored source control program will diminish unwanted chemical discharges, expectations must be realistic regarding the effectiveness of such programs. Source control programs are not assumed to eliminate chemical peaks entirely, though they are important to reduce such occurrences. Specifically, a potable reuse tailored source control program should have the following goals:

1. Minimize discharge of potentially harmful or difficult-to-treat chemical constituents to the wastewater collection system
2. Improve wastewater effluent quality and advanced water treatment performance
3. Provide the public with confidence that the wastewater collection system is being managed with potable reuse in mind

4.1.4 Real Time Monitoring of Water Quality to Detect Perturbations in the Sewershed

Real time monitoring of water quality parameters in the sewershed can help utilities proactively mitigate effects of chemicals peaks. Sewershed water quality monitoring is particularly useful in areas with high presence of industrial dischargers, where chemical peaks are expected to be more prevalent. The following subsections describe monitored parameters that have shown to be effective at detecting chemical peaks in the sewershed.

4.1.4.1 General Water Quality Parameters

Strategic monitoring of key parameters can allow identification of anomalies within a sewershed. Key parameters include conductivity, pH, temperature, and oxidation reduction potential (ORP). Identification of potential chemical peaks is achieved through general water quality parameters and the use of advanced algorithms based on artificial intelligence and machine learning. In scenarios where a sewage network is mapped with these key parameters, it is possible to trace the source of the peak and initiate action in real time. Kando (a company in Tsur Yigal, Israel) has developed water quality dynamic sensors and corresponding analytics to process data and characterize irregularities in the monitored sewershed. Their sensors claim to provide real-time visibility of the wastewater network, detect the source of the event, and provide event prediction to give time to prepare and react to chemical peak events.

4.1.4.2 Volatile Organic Chemicals

The presence of VOCs in the sewershed is of particular concern in areas of industrial dischargers even at low concentration as VOCs may be toxic to the microorganism activity of wastewater treatment plants. As such, an early detection of these compounds can help protect wastewater treatment plants from toxic shocks, which in turn safeguards agencies practicing potable reuse and the quality of their final product water. The following subsections provide descriptions of different methods that have been applied for detection of VOCs in the sewershed, which includes innovative demonstration-scale testing to identify best practices.

Photo-Ionization Detector (PID)

PID is an emerging technology currently used by the PUB for real-time remote monitoring of VOCs in Singapore's sewersheds. This type of sensor employs a UV lamp with a specified output as an ionization source that achieves photo-ionization and a detector that measures current proportional to the concentration of VOCs. A schematic of the PID's working principle is provided in Figure 4-1.

The PID detector does not indicate the presence of specific VOCs, rather, it outputs a bulk VOC concentration. One drawback of the PID is that the output of the ionization source (e.g., UV lamp) must exceed the ionization potential of compounds of interest in order for the compound to be ionized and thus detected by the apparatus. As such, not all VOCs are detectable using this apparatus. For example, if the UV lamp intensity output is 10.6 eV, the detection of methylene chloride would not be possible, as methylene chloride has an ionization energy of 11.22 eV. The ionization potential of some common VOCs is provided in Table 4-4.

PUB has deployed PIDs devices in their sewershed as a proactive source control measure to detect presence of VOCs. These devices have shown to be particularly effective in catchment areas with high presence of industrial waste discharges. The early detection of VOCs in the sewershed is useful for source-tracing and enforcement to those who discharge illicitly.

Table 4-4. Ionization Potential of Specific VOCs.

Compound	Ionization Potential
Styrene	8.40 eV
Toluene	8.82 eV
Benzene	9.24 eV
Methyl Ethyl Ketone	9.54 eV
Acetone	9.70 eV
Isopropyl alcohol	10.12 eV
Formaldehyde	10.88 eV
Methylene Chloride	11.32 eV
Chloroform	11.37 eV

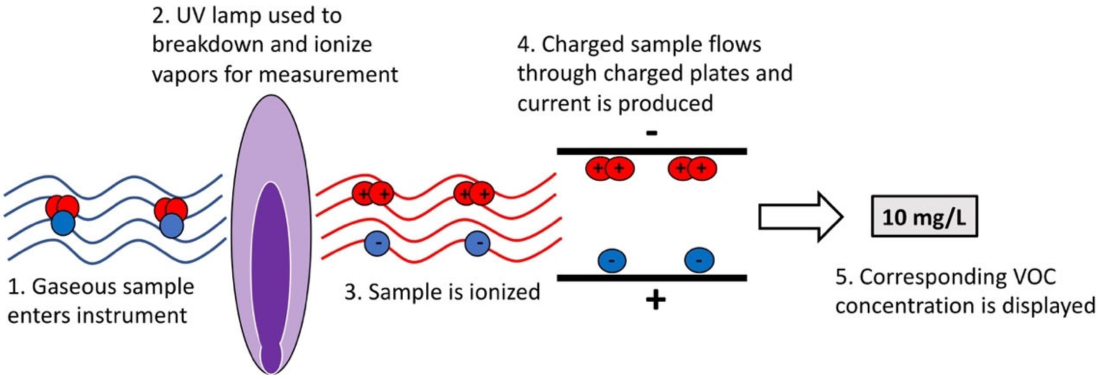

Figure 4-1. Working Principle of a Photo-Ionization Detector for Detecting VOC in the Sewershed.
Source: Courtesy of PUB.

Microbial Electrochemical Sensor (MES)

MES is another method that can be used for detection of VOCs in the sewershed. These sensors use electrochemically-active bacteria (EAB) that can sense toxic chemicals (PUB 2014). These bacteria produce a background signal which can be measured using a biofilm interface. When subjected to VOCs, the background signal decreases since the VOC is toxic to the bacteria. The rate of decrease in the signal depends on the toxicity of the VOC contaminant (or VOC mixture) to the bacteria. This method has been added to PUB's source control efforts as an additional method for detecting VOCs in the sewershed. The working principle of the MES is provided in Figure 4-2. Like PID, one disadvantage of this method is that it does not provide compound-specific information, but rather a bulk assessment of the presence or absence of VOCs. Researchers are evaluating the capability of measuring VOC concentration by using an engineered reporting gene for the EAB (PUB 2014).

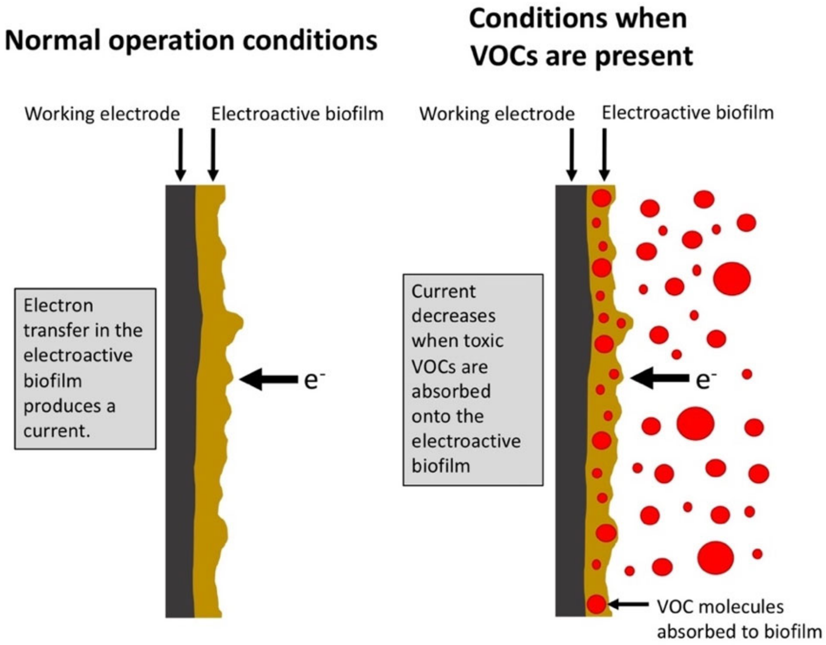

Figure 4-2. Working Principle of a Microbial Electrochemical Sensor for Detecting VOC.
Source: Adapted from PUB 2014.

4.1.5 Instrumentation to Monitor Chemical Peaks during Advanced Treatment

For this evaluation, chemical peaks are identified as abnormal events caused by the intentional or unintentional illicit discharge of chemical-containing waste streams. Chemical peaks can cause the treatment process to deviate from baseline monitoring conditions, such that the height above baseline and duration of the monitored parameter deviation can be used to identify the occurrence of a chemical peak.

Though an effective source control program includes routine monitoring of locations that would possibly indicate the source of a chemical peak, the monitoring frequency of these programs is often insufficient to capture such unexpected, short-lived peaks. Chemical peaks are understood to last on the order of hours to a few days, whereas source control grab sampling occurs on monthly or quarterly basis and thus would not capture chemical peaks that happen in the interim. As such, a more frequent and more automated monitoring method for the advanced treatment process would be desirable to capture chemical peak events. Continuous monitoring is defined as monitoring with a sampling interval of at least once every fifteen minutes (40 CFR § 141.719), which would be sufficient to capture chemical peaks as discussed previously in the Literature Review Document (Chapter 2). The following section describes some options for monitoring chemical peaks using total organic carbon monitoring.

4.1.6 Total Organic Carbon Monitoring

Total organic carbon (TOC) analysis is used to quantify the total amount of organic carbon contained in a sample by converting the organic compounds to a single form while excluding inorganic carbon from the analysis (Crittenden et al. 2012). TOC is a useful parameter as it provides an assessment of the organic concentration in a given water matrix and can be used to identify when conditions deviate from baseline levels due to an interference (such as a chemical peak). The Expert Panel identified high-frequency TOC monitoring analyzers as a feasible option for capturing chemical peaks and would ensure that consumers would not be exposed to a concentration of a contaminant over approximately 100 to 500 µg/L. Based on current knowledge regarding the toxicity of chemicals that can escape FAT and the expected maximum frequency at which the public might be exposed (i.e., a few times per year), the Expert Panel believes this type of exposure would not pose unacceptable human health risks (Olivieri et al. 2016). In addition, TOC is often used as a critical control point (CCP) monitoring device for reverse osmosis (RO) systems, where TOC removal is used as a surrogate for pathogen removal and as a compliance point for meeting recycled water contribution requirements for projects involving indirect potable reuse via groundwater replenishment (OCWD 2015).

For potable reuse applications, it is common practice to place TOC analyzers on the RO feed and RO permeate streams. Though dual-stream TOC analyzers exist, the use of a dual-stream analyzer on RO feed and RO permeate streams would not be recommended as cross contamination of these streams can be an issue[5]. The RO permeate meter is more effective at identifying chemical peaks that pass freely through RO since baseline conditions are very stable and occurrence of a chemical peak would be evident. TOC concentrations in the RO feed are orders of magnitude higher and susceptible to daily and seasonal fluctuations. As such, a small concentration of chemical might be *masked* by the ambient RO feed TOC, even though the presence of this chemical could be classified as a chemical peak when evaluating RO permeate TOC.

Though TOC is an industry accepted method for monitoring RO performance and is used to detect chemical peaks, it is important to understand the different methods of TOC analysis used in TOC analyzers available from different manufacturers. Some TOC methods may be more suitable for

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[5] RO permeate and RO feed TOC are typically 2 orders of magnitude (i.e., 100-fold) apart for typical potable reuse applications

detecting chemical peaks, while others may underestimate the chemical content in the sample which would provide a false-negative.

Chapter 6 (Experimentation to Address Knowledge Gaps) focuses on further evaluating suitability of different commercially available TOC analyzers in terms of detecting and recovering presence of spiked chemicals in potable reuse water matrices (RO permeate and RO feed). Chapter 6 summarizes the report with results of analysis and comparison of the different analyzers/techniques (Appendix A).

4.2 Performance of Water Reclamation Facilities for VOC Removal

A well-functioning water reclamation plant (WRP) serves as an important barrier for removal of VOCs that may otherwise cause higher frequency of chemical peak events at the downstream AWPF practicing potable reuse. Certain VOCs are challenging for removal through FAT. The following sections highlight historical performance of case study WRPs on VOC removal.

4.2.1 VOC Removal across OC San Reclamation Plant No. 1

Routine monitoring of chemical contaminants, such as VOCs, is performed across Orange County Sanitation District (OC San) WWTPs to ensure consistent compliance with state and federal requirements. OC San currently operates two facilities:

1. Reclamation Plant No. 1 (P1), with a secondary treatment capacity of 182 MGD, located in Fountain Valley, CA
2. Treatment Plant No. 2, with a secondary treatment capacity of 150 MGD, located in Huntington Beach, CA

Source water for OC San/OCWD's GWRS is secondary-treated wastewater from the OC San P1. As such, this section covers the historical removal of monitored select VOCs across OC San P1. Table 4-5 provides a description of the OC San P1 processes.

Table 4-5. Summary of Treatment Processes at OC San Reclamation Plant No. 1

Preliminary Treatment	Primary Treatment	Secondary Treatment	Solids Handling
Mechanical bar screens	Advanced Primary using ferric chloride and anionic polymer	Activated sludge operated at NdN (152 MGD capacity)	DAF thickening Anaerobic digestion
Grit Chambers	Primary sedimentation	Trickling filters (30 MGD capacity)	Centrifuge

NdN – biological nitrification/denitrification
DAF – dissolved air flotation

EPA Method 624 is for purgeable organic compounds and covers a subset of compounds recognized as priority pollutants per 40 CFR § 131.38. OC San has conducted routine monitoring of analytes from EPA Method 624 to satisfy permit requirements. Table 4-6 provides a compilation of EPA Method 624 compounds that have been detected in OC San P1 influent between 2008 and 2018 under EPA Method 624.

Table 4-6. EPA Method 624 Compounds Detected in OC San Reclamation Plant No. 1 Influent.
(2008-2018)

Detected VOCs in OC San Reclamation Plant No. 1 influent		
1,2,4-trimethylbenzene	bromochloromethane	m,p-xylenes
1,3,5-trimethylbenzene	bromodichloromethane	methylene chloride
1,4,-dichlorobenzene	bromoform	n-propylbenzene
2-butanone	carbon disulfide	naphthalene
2-chlorotoluene	chloroform	o-xylene
4-isopropyltoluene	dibromochloromethane	sec-butylbenzene
4-methyl-2-pentanone	dibromomethane	styrene
acetone	ethylbenzene	tetrachloroethene
benzene	halomethanes	toluene

Of the 27 compounds historically detected in OC San P1 influent, four were sometimes detected in OC San P1 effluent, which supplies the GWRS influent. They are:

1. Acetone
2. Chloroform
3. Methylene chloride
4. Toluene

Routine monitoring of acetone occurred up to 2011 as part of OC San's NPDES permit. The permit was subsequently updated and no longer requires OC San to monitor for acetone. Of the acetone data available, acetone was the compound present at the highest concentrations in the OC San P1 influent compared to the other VOCs in Table 4-7. Table 4-7 provides average influent and effluent OC San P1 concentrations and reduction percentages of the four compounds sometimes detected in the effluent. OC San laboratory data was used to calculate reduction across P1 based on paired detected samples in both P1 influent and P1 effluent. With exception to methylene chloride, which has an average reduction of 43% across P1, the commonly detected compounds in the effluent have a reduction categorized as intermediate to good (>75%). This indicates that the WWTP supplying the AWPF is an important barrier for the reduction of VOCs.

Table 4-7. Concentration Range and Average Reduction for Relevant Compounds at OC San P1 (OC San Data).

Compound	P1 Influent	P1 Effluent	Reduction across P1[1]
Acetone	91 – 12,800 µg/L (n = 43)	5 – 167 µg/L (n = 43, 33% above ND)	96.6% (n = 14)
Chloroform	1.71 µg/L – 14.6 µg/L (n = 133)	0.39 – 3.36 µg/L (n = 133, 96% above ND)	79.2% (n = 128)
Methylene chloride	0.63 – 16.4 µg/L (n = 121)	0.65 – 4.17 µg/L (n = 121, 13% above ND)	43.1% (n = 16)
Toluene	0.5 – 19.1 µg/L (n = 119)	0.01 – 0.40 µg/L (n = 119, 25% above ND)	94.1% (n = 30)

n = data points (detects and non-detects) ND = non-detect
Range of concentrations shown only consider samples above detection limit
[1] Average reduction percentage based on paired influent and effluent samples. Only samples above detection limit were considered in the calculation of paired reduction percentage.

Additional OCWD laboratory data on the occurrence of the four compounds in OCWD GWRS influent (GWRS Q1) is provided in Table 4-8. The data reported considers OCWD's typical calculation, where non-detect (ND) results are 10% of reportable detection limit (RDL) and trace results (TR) are 50% of RDL.

Table 4-8. GWRS Influent Statistics of Select Compounds (OCWD Data).

Compound	Min	Median	Max	STDEV	Detect Count	n
Acetone	1.0 µg/L	1.0 µg/L	275 µg/L	40 µg/L	18	196
Chloroform	0.25 µg/L	0.25 µg/L	1.0 µg/L	0.20 µg/L	76	79
Methylene chloride	0.05 µg/L	0.05 µg/L	2.3 µg/L	0.37 µg/L	29	79
Toluene	0.05 µg/L	0.05 µg/L	1.0 µg/L	0.18 µg/L	1	79

Note: for statistics, OCWD considers ND results to be 10% of RDL and TR to be 50% of RDL.
n = data points (detect and non-detects)

4.2.2 VOC Removal across City of San Diego North City Water Reclamation Plant

Routine monitoring of chemical contaminants, such as VOCs, is performed at City of San Diego North City Water Reclamation Plant (NCWRP) to ensure consistent compliance with state and federal requirements. The NCWRP is scheduled for expansion from current 30 MGD capacity to 54 MGD to provide feed water to the future 30 MGD North City Pure Water Facility while continuing to produce recycled water that meets California's recycled water requirements.

The reclaimed water undergoes treatment consisting of primary, secondary, and tertiary treatment. Primary treatment consists of bar screens, grit removal, and conventional primary sedimentation. Following that, flow undergoes biological nitrification and partial denitrification in a Modified Ludzack-Ettinger secondary process. Tertiary treatment for reclaimed water includes filtration with anthracite media, demineralization with electrodialysis reversal, and chlorine disinfection. An aerial layout and process flow diagram for the NCWRP treatment processes are shown in Figure 4-3 and Figure 4-4.

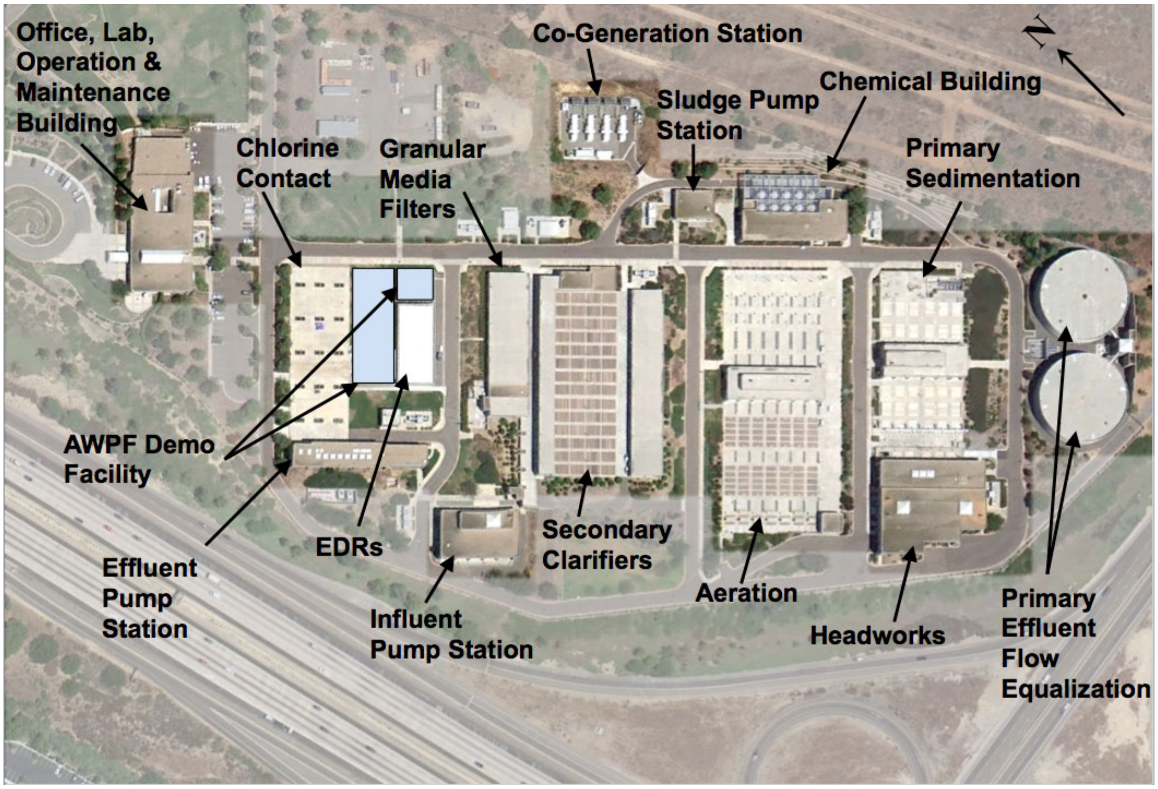

Figure 4-3. Aerial View of North City Water Reclamation Plant.

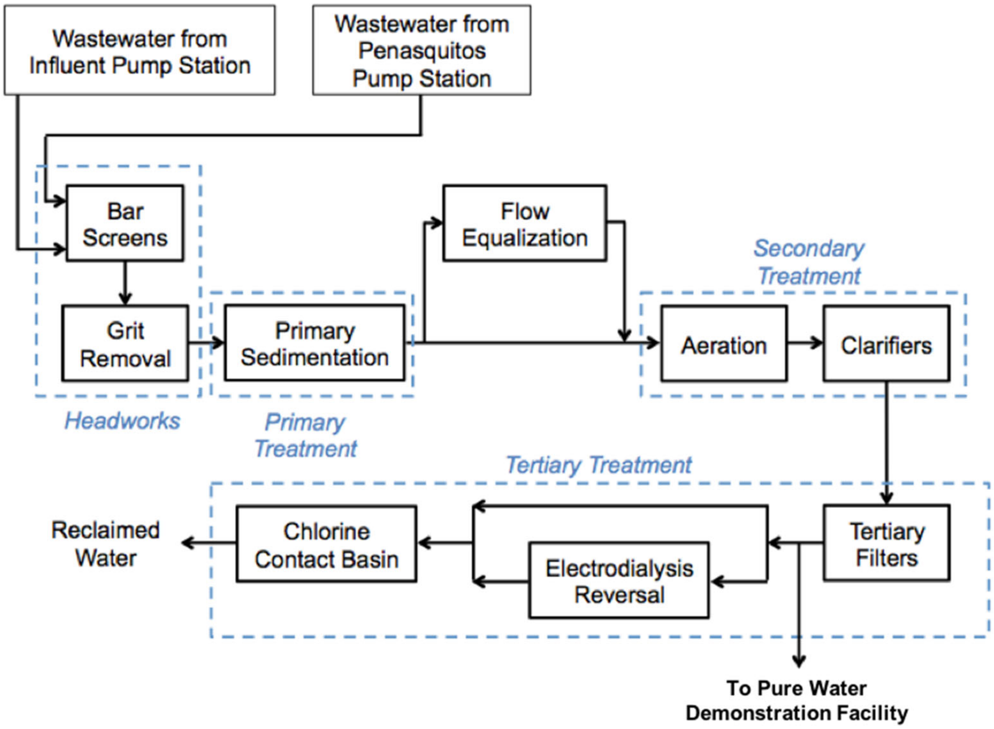

Figure 4-4. North City Water Reclamation Plant Process Flow Diagram.

NCWRP routinely samples 50 VOCs on a quarterly basis. Table 4-9 provides a compilation of the monitored compounds been detected in NCWRP primary effluent between 2010 and 2018 and provides average primary effluent and reclaimed water concentrations as well as paired removal percentage. Of the nine compounds commonly detected in primary effluent, four compounds were detected in the reclaimed water above method detection limit (i.e., acetone, meta, para-xylenes, methylene chloride, and ortho-xylenes). Average acetone removal across NCWRP can be categorized as excellent, as an average removal of 98.8%. Only one out of 34 sampling events detected xylenes in the reclaimed water, when removal was 88.1% and 78.9% for meta, para-xylenes and ortho-xylenes, respectively. Methylene chloride was detected above the detection limit in the reclaimed water, such that removal was calculated to be 74.4%. Similar to OC San Plant 1, VOC removal across NCWRP indicates that the supplying water reclamation is an important barrier to reduce VOC loading to the downstream AWPF.

Table 4-9. Average Concentrations at Select Locations and Reduction of Compounds at NCWRP.
Data from 2010-2018

Compound	Primary Effluent	Reclaimed Water	Reduction across NCWRP
2-Butanone (MEK)	9.1 µg/L	< 6.3 µg/L	≥ 29.7% (n = 26)
Acetone	592 µg/L	8.1 µg/L	98.8% (n = 33)
Carbon Disulfide	2.8 µg/L	< 0.6 µg/L	≥ 75.4% (n = 32)
Ethylbenzene	0.7 µg/L	< 0.3 µg/L	≥ 41.3% (n = 5)
meta, para- xylenes	2.6 µg/L	0.84 µg/L[1]	88.1% (n = 1)
Methylene chloride	4.2 µg/L	0.9 µg/L	74.4% (n = 26)
ortho-xylene	1.4 µg/L	0.63 µg/L[2]	78.9% (n = 1)
Styrene	2.6 µg/L	< 0.3 µg/L	≥ 88.4% (n = 1)
Toluene	4.8 µg/L	< 0.4 µg/L	≥ 80.2% (n = 32)

Note: average values shown.
Reported average reduction percentage is based on paired primary effluent and reclaimed water samples.
“n” represent number of data points.
1 – only one sample detected above detection limit of 0.6 µg/L when feed concentration was 7.05 µg/L.
2 – only one sample detected above detection limit of 0.4 µg/L when feed concentration was 2.99 µg/L.

4.3 Documented Illicit Chemical Discharges at Case Study Utilities

4.3.1 Defining an Illicit Chemical Discharge

For the purpose of evaluating impacts of chemical peaks, an illicit chemical discharge can be defined as the illicit introduction of chemicals to a sewershed. There are different outcomes that can occur from an illicit chemical discharge:

1. For a WWTP:
    a. The illicit chemical discharge causes a WWTP NPDES violation due to either pass through and/or interference with treatment processes. This would be a non-compliant discharge, or,
    b. The illicit chemical discharge does not cause a WWTP NPDES violation
2. For an AWPF:
    a. The illicit chemical discharge from either 1a or 1b cause a chemical peak, or,
    b. The illicit chemical discharge from either 1a or 1b is effectively removed by the AWPF

4.3.2 Documented Illicit Chemical Discharges at Orange County Water District

The GWRS is a 100 MGD AWPF and joint effort between OCWD and OC San that produces highly-treated recycled water for groundwater replenishment and to supply a seawater intrusion barrier. Over the past eleven years, the GWRS has gathered extensive amounts of data that have substantiated its treatment efficacy. Online TOC data is among the parameters monitored. GWRS currently has redundant (dual) monitors on both the RO feed and RO permeate streams. The TOC analyzers used at GWRS are supplied by Sievers/Suez (model M5310C and 5310C). These online analyzers provide measurements every 2 minutes, providing 360 data points per day. The TOC analyzers at GWRS have served as an online tool to detect when the RO system deviates from baseline conditions. The following subsections describe occurrences where TOC was used as a tool to indicate the presence of chemical peaks.

4.3.2.1 2013 GWRS Acetone Event

The 2013 acetone event at the GWRS has been extensively described in previous documents, including facility annual reports (OCWD 2013a), journal articles (Patel 2014), and the California Expert Panel Report on DPR feasibility (Olivieri et al. 2016). In addition, OCWD reported this occurrence to the California Regional Water Quality Control Board (RWQCB) shortly after the event (OCWD 2013b).

At approximately 5:48 PM on February 17, 2013, the online TOC values from the RO feed (at this date, only a single TOC monitor not dual monitors) began to increase from typical concentrations. The elevated TOC readings remained until approximately 12:00 PM on February 19, 2013, returning to normal levels thereafter. A peak TOC value of approximately 21.4 mg/L in the RO feed was recorded at around 3:28 PM on February 18, 2013. A corresponding increase in the RO permeate online TOC analyzer readings was also observed during this period. The increase began at approximately 5:17 PM on February 17, 2013, and reached a peak value of approximately 7.0 mg/L at 4:42 PM on February 18, 2013. RO permeate TOC readings were reestablished at background levels at approximately 12:00 PM on February 19, 2013. Figure 4-5 provides online TOC readings from the RO feed and RO permeate between February 17 – 20, 2013, which captures the extent and duration of the TOC peak during this event.

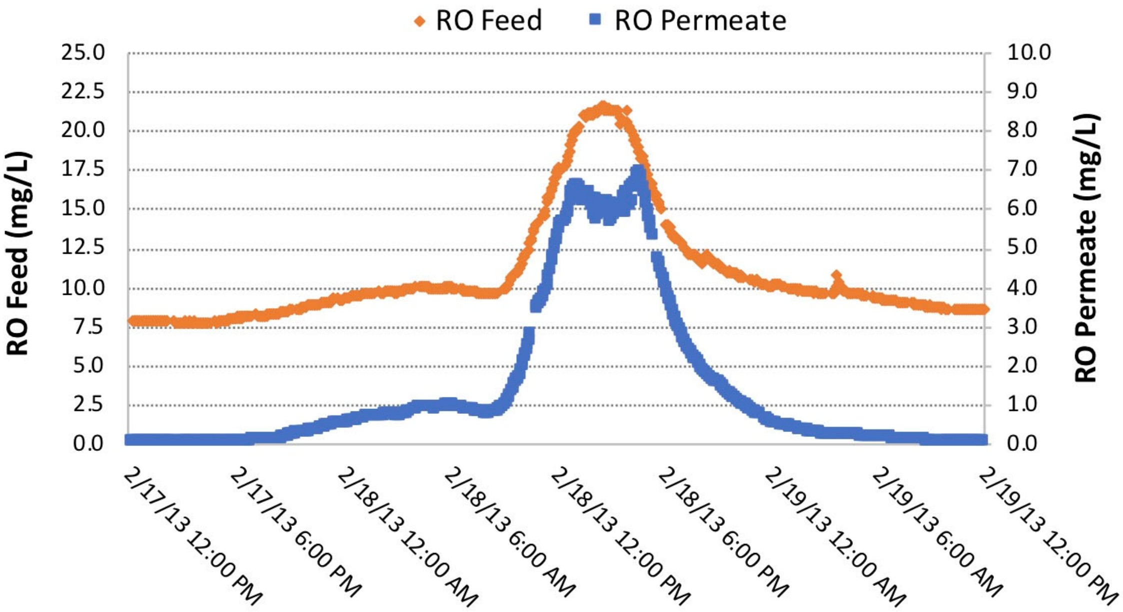

Figure 4-5. GWRS TOC Monitoring during 2013 Acetone Event (February 17–20, 2013).

During this event, OCWD collected samples to investigate compound(s) responsible for the elevated TOC levels. The tests performed included EPA 524.2 (VOC), EPA 525.2 (SOC), as well as OCWD's methods targeting 1,4-dioxane and NDMA. A review of the resulting data revealed that only acetone was detected at elevated concentrations. A sample from the RO permeate was collected at 6:00AM on February 18, 2013, and had an acetone concentration of 1,410 µg/L. At this time, a sample was also measured for TOC using method EPA 415.3 and had a TOC concentration of 1.18 mg/L. Considering acetone's carbon content of 62%, acetone represented 78% of the TOC in the RO permeate (Table 4-10). Samples were also collected from the RO feed and measured for acetone and TOC. Similar to the RO permeate, the presence of acetone agreed with the elevated TOC levels in the RO feed where acetone was responsible for approximately 86% of the elevated TOC in the feed (as captured in Table 4-10). Since acetone was the only constituent detected at an elevated concentration, it was deduced that acetone was responsible for the elevated TOC concentrations during this 2013 chemical peak event. This seminal event showed that TOC meters are effective in detecting a chemical peak in the RO feed and RO permeate. If TOC meters were not available, it is unlikely that a regular sampling program of the RO permeate would have identified this chemical peak.

Table 4-10. TOC and Acetone Grab Sample Results during 2013 GWRS Acetone Event.

Sample Date	Sample Location	EPA 524.2 Acetone	Theoretical TOC from Acetone[1]	EPA 415.3 TOC	Baseline TOC[2]	Acetone Contribution to Elevated TOC[3]
2/18/2013 6:00AM	RO Feed	1,940 µg/L	1.2 mg/L	9.39 mg/L	~ 8.0 mg/L	~ 86%
	RO Permeate	1,410 µg/L	0.9 mg/L	1.18 mg/L	~ 0.025 mg/L	~ 78%

[1] Acetone carbon contribution is approximately 62%

[2] From online TOC data preceding the acetone event

[3] Baseline TOC subtracted from EPA 415.3 TOC used to calculate % acetone that contributed to elevated TOC (e.g., for RO feed → 1.2 mg/L / (9.39 mg/L – 8.0 mg/L) = 86%

Further analysis of the TOC online data from the 2013 GWRS event was performed to estimate the theoretical mass (and volume) of chemical discharged to the sewershed to have caused the TOC peak that was captured. This analysis included the following assumptions and procedures:

1. The mass of acetone in the GWRS influent (WWTP effluent) was estimated by calculating the mass under the TOC feed curve using the known carbon-contribution of acetone, RO feed flow rate, and time.
    a. Acetone has a carbon-contribution of 62%.
    b. GWRS RO feed flow was 82 MGD in 2013 (assuming 85% recovery and 75 MGD RO product flow).
    c. RO feed TOC data from the 2013 peak was used estimate mass under the curve (timeframe: 2/17/2013 4PM – 2/19/2013 11AM).
    d. Baseline RO feed TOC (approximately 8 mg/L) was subtracted during peak event, such that only TOC due to acetone was accounted for.
    e. The maximum RO feed concentration observed during 2013 peak event was 21.4 mg/L at 3:30 PM 2/18/2013.
2. The mass of acetone in RO feed was *backcalculated* to determine the mass at the WWTP influent, which indicates the amount discharged to the sewershed. For this, it was necessary to assume a particular acetone removal across the WWTP.
    a. The historical average mass-based acetone removal across OC San P1 is reported to be 97% (OCWD 2013a) (average influent and effluent concentrations of 2,218 µg/L and 12 µg/L, respectively).
    b. For this 2013 event, a lower reduction of 50-90% was assumed as the range since acetone concentration was much higher than during baseline conditions.
    c. This assumption was made considering 500 mg/L is toxic to microorganisms when biooxidation of acetone by activated sludge occurs (Gerhold and Malaney 1966).

From this analysis, the volume of acetone discharged to the sewer system is estimated to be ~1,900-9,500 gallons (50% acetone removal and 90% acetone removal, respectively), or approximately up to two conventional tanker trucks of 5,000 gal each.

In terms of concentration, the estimated maximum acetone concentration at OC San P1 influent would have been 216 mg/L based on P1 plant-wide removal of 90% (or 43 mg/L if a P1 plant-wide acetone removal of 50% were assumed).

OC San and OCWD were unable to determine the source of the 2013 acetone event. The GWRS permit contains no specific regulatory limit for acetone, and there is no federal EPA or State of California Maximum Contaminant Level (MCL). Nonetheless, OCWD was mandated to submit reasons and corrective actions to DDW within 60 days of this acetone event. At no time did GWRS's 20-sample running average[6] approach the 0.5 mg/L permit TOC limit that would require the suspension of recycled water recharge and injection. In addition, there is currently no drinking water regulatory limit for acetone in the United States[7] and experts concluded regarding these incidences that 'acetone features low acute and chronic toxicity and is not considered a carcinogen' (OCWD 2013a).

GWRS staff undertook a series of response actions following the 2013 acetone event, such as:

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[6] Represents the running average of 20-samples based on daily composites

[7] The State of Massachusetts has set an Office of Research Standards Guidance Level (ORSGL) of 6,300 µg/L for acetone based upon an EPA IRIS Reference Dose (RdD). No concentration detected by OCWD at the GWRS facility has been in excess of the Massachusetts ORSGL (OCWD 2013b).

1. Review of the operation and maintenance calibration records of the online TOC analyzers.
    a. The review indicated that all analyzers were functioning properly.
2. Review and inspection of the GWRS facility and maintenance processes for possible sources of acetone.
    a. The review did not indicate any likely sources.
3. Review of the Operational Optimization Plan (OOP) and development of more formal response criteria in events of elevated TOC levels.
    a. Specifically, the permeate TOC upper control limit was lowered from 0.35-0.45 mg/L to 0.1 mg/L. Additionally, different response levels based on TOC values were developed as shown in Table 4-11. Information regarding analysis performed to arrive at the revised upper control limit of 0.1 mg/L is provided in Gonzalez et al. (2015).
4. Inspection of a sewer discharge permittee that used acetone and had a previous discharge violation several years prior in which inventory acetone was dumped to the sewer.
    a. During the inspection, the permittee stated that acetone was no longer being used on-site.

Table 4-11. Updated RO Permeate TOC Response Protocols after 2013 Acetone OCWD Event.

Response Level	TOC Value (mg/L)	Duration	Response Action
I	0.10	1 hour	Investigate
II	3.00	1 hour	Shutdown
II	1.50	1 day	Shutdown
II	0.50	4 days	Shutdown
II	0.45	20 days	Shutdown

Based on the updated TOC response protocols (Table 4-11), another event like the 2013 acetone discharge would lead OCWD staff to shut down operations, in an abundance of caution.

4.3.2.2 October 2018 GWRS Chemical Peak I

On October 9, 2018, around 11:30PM, the GWRS RO permeate TOC rose above its baseline concentration to a maximum value of approximately 0.25 mg/L (Figure 4-6). Before this peak since March 2018, GWRS has been using redundant online TOC analyzers and the peak was captured on both permeate TOC analyzers. An increase in either RO feed TOC analyzer was not apparent – due to the lesser extent of this peak compared to that recorded in 2013, such that the baseline feed TOC “masked” the peak. In fact, close inspection of the RO feed data at this time reveals that the slight increase in RO feed (0.3 mg/L) was within range of normal diurnal variation of TOC. Using the new response protocols (Table 4-11), this event would qualify as Response Level “I”. Based on OCWD’s updated response protocols from 2013 and consistent with the new protocol, OCWD staff collected samples during the elevated TOC event. Samples were analyzed using the EPA 524.2 method and found to contain 215 µg/L of acetone in the RO permeate. The samples were collected at 1:06 AM when the TOC was 250 µg/L. Considering an acetone carbon contribution of 62%, the acetone TOC contribution would have been 133 µg/L which approaches the elevated TOC readings at the time of sample collection.

At a later date, OCWD was informed about the unintentional discharge of 700 gallons of isopropyl alcohol by a local food and drug manufacturer due to a significant operator error around 8:00AM on October 8, 2018 (the morning prior to the October 9th TOC spike). Isopropyl alcohol is readily used in the cleaning of food or pharmaceutical preparation equipment, and can biologically oxidize to acetone, particularly under oxic conditions (Schmidt et al. 2004). The manufacturer has since been directed to implement corrective actions to avoid future slug discharges of isopropyl alcohol.

For the present analysis for this case study, further evaluation of the RO permeate TOC was performed for this event as well. The area under the TOC curve corresponds to a volume of ~600 gallons of acetone (or ~590 gallons of isopropyl based on specific gravity ratios), which is over an order of magnitude less than during the 2013 event. This approaches the volume of isopropyl alcohol reported to have been discharged by the food and drug manufacturer. A 25% removal across the RO membrane was assumed for the present analysis based on results reported elsewhere (Tackaert et al. 2019) and a 97% reduction was assumed across the OC San P1. The historical acetone reduction of 97% was assumed since the maximum acetone concentration (i.e., ~10 mg/L) was within the range of those historically observed at the OC San P1 influent (refer to Table 4-7) and was unlikely to have toxic effects on the biological treatment system.

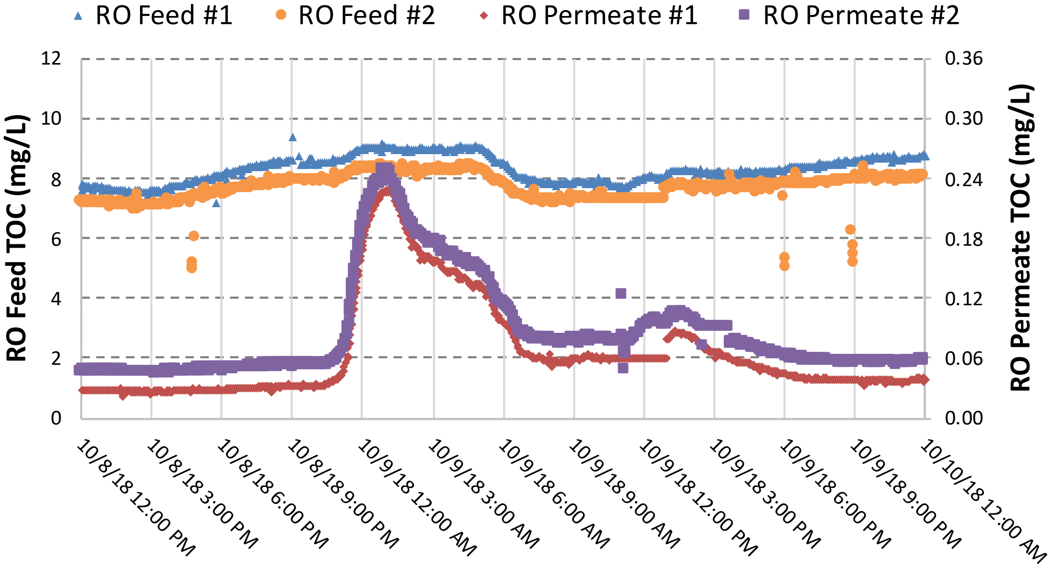

Figure 4-6. OCWD TOC Monitoring for First October 2018 Acetone Event (October 9, 2018).

4.3.2.3 October 2018 GWRS Chemical Peak II

A second chemical peak was recorded later during the month of October 2018 at GWRS. At approximately 5 PM on October 24, 2018, both of the dual RO permeate TOC analyzers reached a peak value of around 0.24 mg/L, relative to a baseline of 0.05 mg/L. Similar to the October 9, 2018, peak, RO feed TOC values remained within the daily variance recorded for the days preceding and following this chemical peak. Figure 4-7 captures the RO feed and RO permeate TOC monitoring during this event. An investigative sample was collected at 6:20 PM, coinciding with the approximate maximum value of the peak, and 226 µg/L of acetone was measured. At a carbon contribution of 62%, the TOC contribution from acetone would have been 0.14 mg/L. Accounting for a baseline of 0.05 mg/L, this peak appears to have been caused mainly by acetone. Unlike the earlier October 2018 event, the source for this event was not determined.

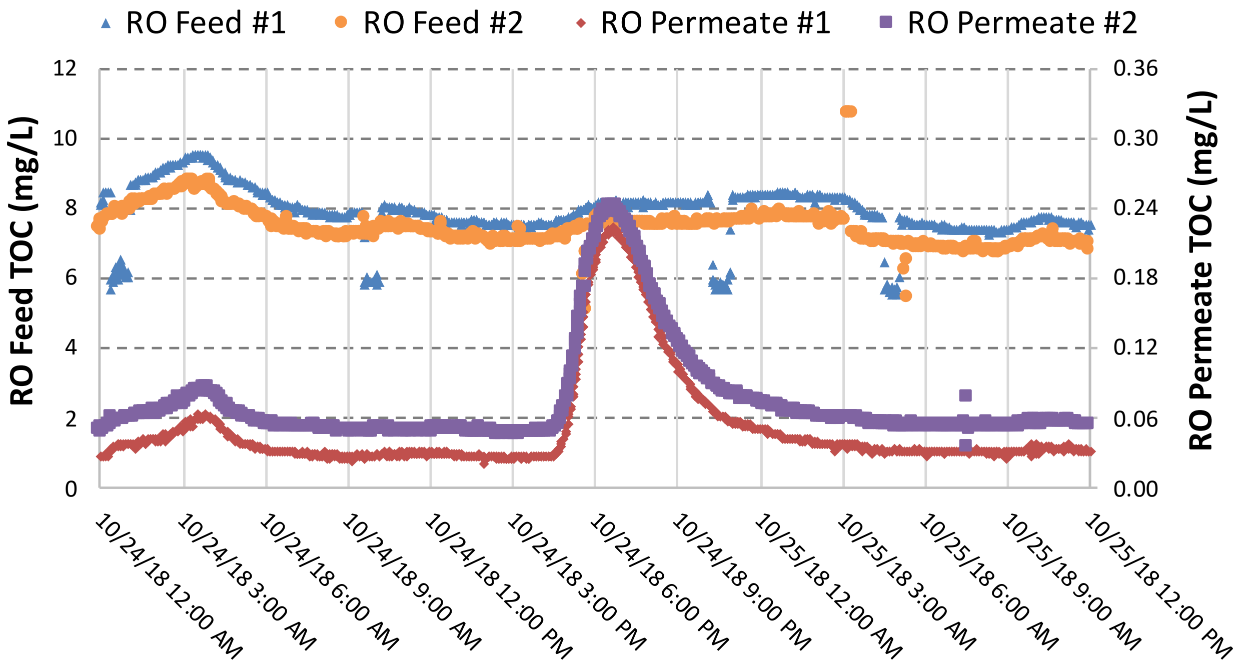

Figure 4-7. OCWD TOC Monitoring for Second October 2018 Acetone Event (October 24, 2018).

4.3.3 Chemical Challenge Tests at City of San Diego's PWDF

The City of San Diego (City) operates several major facilities to treat wastewater:

1. North City Water Reclamation Plant (NCWRP) with 30 MGD capacity
2. Point Loma Wastewater Treatment Plant (PLWTP) with 175 MGD capacity
3. South Bay Water Reclamation Plant (SBWRP) with 15 MGD capacity

In addition, the City operates the 1 MGD Pure Water Demonstration Facility (PWDF). The PWDF receives tertiary treated effluent from NCWRP to produce highly-treated recycled water using a five-step water treatment process of ozonation (O_3), biological activated carbon filters (BAC), membrane filtration (MF), reverse osmosis (RO) and ultraviolet light disinfection with a chlorine based ultraviolet advanced oxidation process (AOP). The PWDF has been operational since 2011 and has served as proving grounds for the technologies that will be used to purify recycled water to produce high-quality drinking water as part of the City's Pure Water Program. The City's Pure Water Program is expected to produce 1/3 of San Diego's water supply locally by 2035 using technologies similar to those employed at the PWDF.

An important aspect of the PWDF has been to develop and evaluate monitoring tools that confirm performance and indicate when process excursions and/or failures occur. Within this scope, the evaluation of TOC monitors and their ability to identify chemical peaks and process deviations has been part of the facility's testing efforts. Figure 4-8 provides over a year of online TOC monitoring of the RO permeate from the PWDF. Online monitoring shows that TOC has consistently been under 0.1 mg/L. Two events are highlighted in the figure where deviations in TOC deviation were observed. A decrease in TOC permeate was observed in early April 2018 after the RO system was brought back online after being shut down for several months due to on-site testing. After initial troubleshooting, the analyzer readings were restored to baseline values. In late June 2018, the RO permeate TOC slightly increased. This increase was process related due to an artifact of the demonstration facility. Specifically, a portion of BAC influent overflowed due to high headloss and was combined with BAC effluent, such that RO permeate TOC increased slightly. This event is specific to the demonstration facility, which has no redundant filters; in other words, a full-scale facility would shut down due to high level (or high headloss) alarm and any BAC overflow would be treated as waste.

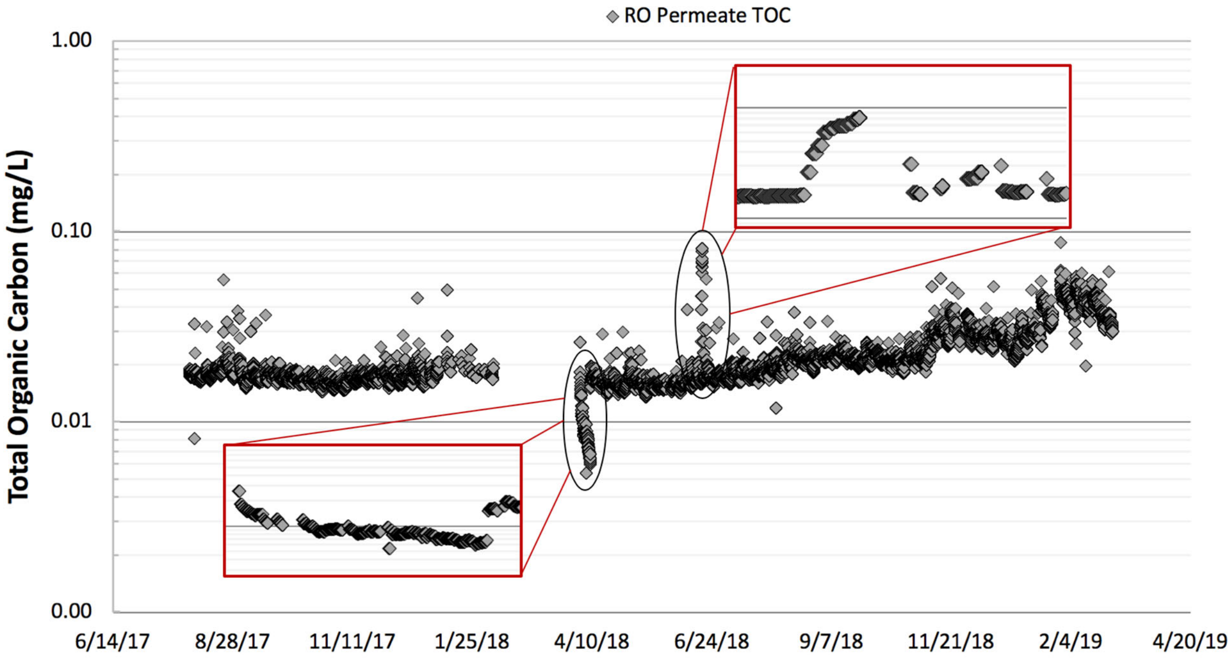

Figure 4-8. Online TOC Monitoring at City of San Diego Pure Water Demonstration Facility.

In addition to regular monitoring, the demonstration facility has undergone a number of challenge tests to evaluate process robustness. Such tests also served to document treatment robustness due to chemical peaks and capability of monitoring tools used at the PWDF.
These system-wide chemical challenge tests were performed at the PWDF between 2015 and 2016. A full description of this study is provided in Tackaert et al. (2019). These challenge tests consisted of spiking neutral low molecular weight compounds known to be challenging for advanced treatment at the inlet of two treatment train configurations: O_3/BAC-MF/UF-RO-AOP and MF/UF-RO-AOP. The spiked compounds and influent concentrations of these compounds during these challenge tests were:

1. 1,4-dioxane (907 µg/L)
2. Acetone (2,667 µg/L)
3. Formaldehyde (307 µg/L)
4. N-nitrosodimethylamine (NDMA) (550 µg/L)

These challenge tests served to benchmark these different treatment processes. All product water was diverted to waste during these experiments. The chemical spike was continuously fed during the experiments and sampling occurred when steady-state conditions were achieved (based on system-wide hydraulic retention time, HRT, and TOC analyzers). Compound reduction across each barrier as well as cumulative reduction is provided in Table 4-12. MF/UF is not reported as this process did not contribute to the reduction of these low molecular weight compounds. The majority of the reduction of acetone and formaldehyde occurred during BAC, which suggests the effectiveness of biologically active barrier to control chemical peaks. When O_3/BAC was not included as pretreatment to MF/UF-RO-AOP, the cumulative reduction of compounds was limited to 83% for 1,4-dioxane, 15% for acetone, 10% for formaldehyde, and 98.5% for NDMA.

Table 4-12. Reduction and Average Effluent Concentration of Spiked Compounds during Challenge Tests at PWDF.

Compound	Influent	O$_3$	BAC	RO	AOP[1]	Cumulative O$_3$/BAC-MF/UF-RO-AOP	Cumulative MF/UF-RO-AOP only[4]
1,4-dioxane	907 µg/L	62% 343 µg/L	28% 247 µg/L	75% 65 µg/L	93% 5 µg/L	99.5% 5 µg/L	83% 157 µg/L
Acetone	2,667 µg/L	2% 2,567 µg/L	50% 1,267 µg/L	25% 1,100 µg/L[2]	20% 880 µg/L	66% 880 µg/L	15% 2,367 µg/L
Formaldehyde	307 µg/L	(24%) 380 µg/L	97% 13 µg/L	*(38%)* 18 µg/L	*(22%)* 22 µg/L	93% 22 µg/L	10% 297 µg/L
NDMA	550 ng/L	*Ineffective* 533 ng/L	71% 153 ng/L	24% 157 ng/L[3]	98% 3 ng/L	99.5% 3 ng/L	98.5% 5 ng/L

Note: MF not shown as it was ineffective in removal of spiked compounds

Value in parentheses represent concentration increase. Extent of formaldehyde increase through RO and AOP was not observed during ambient conditions.

1 – AOP configured as UV/HOCl with 3 mg/L as Cl$_2$

2 – RO feed average acetone concentration was 1,467 µg/L

3 – RO feed average NDMA concentration was 207 ng/L

4 – For comparison purposes only. Influent concentrations for MF/UF-RO-AOP challenge test were slightly different than for O$_3$/BAC-MF/UF-RO-AOP challenge test. AOP configured as UV/H2O2 with 3 mg/L H2O2 for MF/UF0RO-AOP challenge test.

Based on challenge test data and considering contaminant notification limits (NL) and TOC limits, the O$_3$/BAC-MF/UF-RO-AOP can theoretically treat up to[8]:

1. 200 µg/L of 1,4-dioxane (NL = 1 µg/L)
2. 1.47 mg/L of acetone (TOC limit = 0.50 mg/L)[9]
3. 1,400 µg/L of formaldehyde (NL = 100 µg/L)
4. 2,000 ng/L of NDMA (NL = 10 ng/L)

In contrast, for potable reuse treatment trains employing MF/UF-RO-AOP without O$_3$/BAC pretreatment, the theoretical maximum load concentration for these compounds is considerably less. The addition of O$_3$/BAC as pretreatment to RO-AOP provided additional protection against all the spiked contaminants, indicating that robust treatment trains are able to handle greater contaminant loading in events of chemical peaks (such as illicit chemical discharges).

During the challenge tests, TOC analyzers were used to monitor the presence of chemical compounds at three locations: ozone influent, BAC effluent, and RO permeate. The ozone influent and BAC effluent analyzer used was a dual-stream on-line Sievers M5310 C, whereas the RO permeate TOC analyzer was Sievers 5310 C. Both analyzers use UV/persulfate and membrane conductivity to measure oxidizable carbon and sample acidification to measure inorganic carbon. The TOC monitoring during the challenge test is shown in Figure 4-9. The increase in TOC was visible once the spike commenced. The increase in RO permeate TOC took longer to show an increase due to the HRT between the BAC and RO process (approximately 40 minutes at this facility). In order to measure the effectiveness of the TOC analyzers in recovering the spiked compounds, a mass balance was performed using the measured TOC and compound concentrations. Table 4-13 provides the methodology applied for measuring TOC meter

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[8] These theoretical limits are not universal. They were site-specific based on tested facility, which can be influenced by source water quality and BAC age/performance, as well, for example.

[9] There are no federal EPA or State of California Maximum Contaminant Level (MCL) for acetone. The reported odor threshold for acetone in water is 20 mg/L.

recovery. Overall, all three locations provided a TOC recovery within ± 15% relative to spiked compound concentration and background TOC. This indicates that the TOC analyzers used successfully recovered the spiked compounds and clearly indicated the occurrence of a chemical peak.

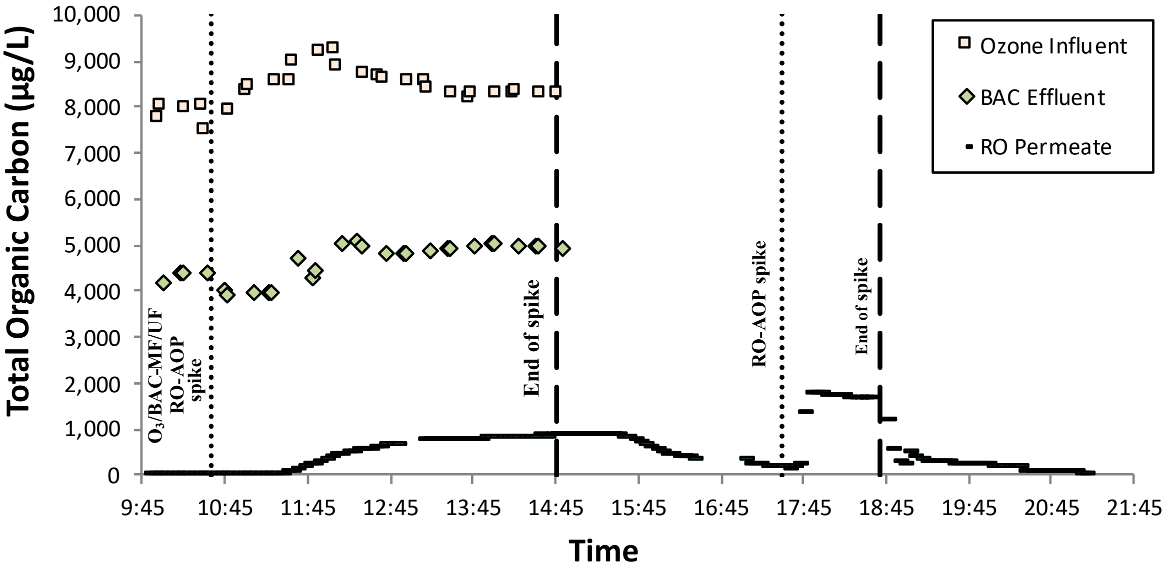


Figure 4-9. Online TOC Monitoring during Chemical Challenge Tests at PWDF.

Source: Adapted from Tackaert et al. 2019.

Table 4-13. TOC Analyzer Mass Balance during Challenge Testing at PWDF.

Parameter	Carbon content (%)	Ozone Influent (µg/L)	BAC Effluent (µg/L)	RO Permeate (µg/L)
Formaldehyde	40%	307	12	18
NDMA	32%	0.55	0.153	0.157
1,4-dioxane	55%	907	247	65
Acetone	62%	2,667	1,267	1,100
Background TOC[1]	-	7,730	4,200	33
Theoretical TOC[2]	-	10,003	5,126	758
Actual TOC[3]	-	8,535	4,990	850
TOC Meter Recovery[4]	**-**	**85%**	**97%**	**112%**

1 – baseline TOC prior to the spike
2 – theoretical TOC = background TOC + Σ [carbon-content of spiked chemicals]
3 – steady-state TOC during challenge test
4 – actual TOC / theoretical TOC

4.3.4 Documented Illicit Chemical Discharges at Singapore PUB

The Public Utilities Board (PUB) is Singapore's national water agency that manages and regulates Singapore's water supply, catchment, and reclamation.

PUB has been increasing its supply of local water sources over the years. Currently, PUB supplies up to 40% of demand using NEWater and up to 25% from desalinated water. By 2060, PUB is expected to increase NEWater capacity to supply 55% of the demand and up to 30% from desalinated water. Together, these two local sources will supply up to 85% of Singapore's future water needs.

Currently, NEWater is mainly used in wafer fabrication plants, industrial estates, and commercial buildings for cooling and industrial processes. During dry periods, NEWater is added to PUB's drinking water reservoirs to blend with raw water. There are a total of five NEWater plants which together feature a capacity of 175 MGD:

1. Changi NEWater Plant 1 + 2 – 50 MGD + 50 MGD capacity
2. Ulu Pandan NEWater Plant – 35 MGD capacity
3. Kranji NEWater Plant – 22 MGD capacity
4. Bedok NEWater Plant – 18 MGD capacity

PUB also owns four WRPs (wastewater treatment plants) which together have a total capacity of 360 MGD:

1. Changi Water Reclamation Plant (CWRP) – 202 MGD capacity
2. Ulu Pandan Water Reclamation Plant (UPWRP) – 79 MGD capacity
3. Kranji Water Reclamation Plant (KWRP) – 34 MGD capacity
4. Jurong Water Reclamation Plant (JWRP) – 45 MGD capacity

Figure 4-10 provides the location of these WRPs and their respective capacity. The map also distinguishes the catchment areas relative to their WRPs and risk rating based on presence of high-risk dischargers. The JWRP catchment area has the highest presence of high-risk dischargers and is currently not serving a NEWater facility. PUB is in the process of constructing an additional conveyance system dedicated for the southwestern region of Singapore covering parts of the Ulu Pandan and Jurong catchment area. This new conveyance system (named Deep Tunnel Sewerage System Phase 2 [DTSS Phase 2]) will also include the decommissioning of Jurong WRP and Ulu Pandan WRP, which will be replaced with Tuas WRP and Tuas NEWater facility. The Tuas WRP will treat industrial and domestic sewerage separately, which will then be conveyed separately for supply. The Tuas WRP will have an initial capacity of 176 MGD (143 MGD for domestic sewerage and 33 MGD for industrial sewerage). The NEWater facility will have an initial treatment capacity of 22 MGD. Expected completion for the project is 2025. The following subsections describe documented events of illicit chemical discharges and their impact at select PUB WRP and NEWater facilities.

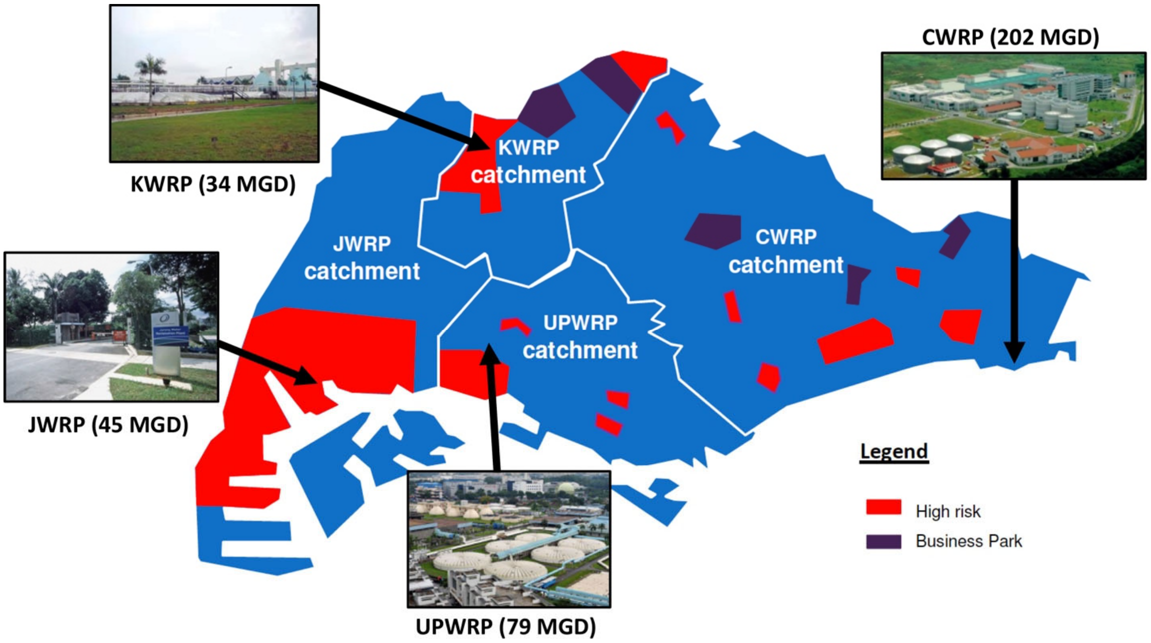


Figure 4-10. Location of PUB Water Reclamation Plants.
As of 2019.

4.3.4.1 Documented Illicit Chemical Discharges at Jurong WRP

JWRP's catchment area has a high presence of industrial dischargers that are categorized as high risk. PUB categorizes dischargers based on track record and risk associated with the discharger's sewerage. The grouping and basis for each group is provided in Table 4-14. PUB actively surveils up to 5,000 dischargers.

In order to prevent and deter illicit chemical discharges in the JWRP catchment, PUB has employed close monitoring of high-risk dischargers. This has been achieved through the installation of VOC monitoring units in the sewershed. The VOC monitoring units have auto-sampling capabilities and are useful for source tracing of illicit chemical discharges.

There are currently 10 VOC monitoring units in the JWRP catchment that are strategically located for source tracing of VOC illicit discharges. The installation of 32 additional VOC monitoring units in the JWRP catchment is planned. Figure 4-11 shows the distribution of current and future VOC monitoring units relative to the location of the industrial dischargers within JWRP sub-catchment areas (i.e., Tuas View, Tuas, Pioneer Sector, Benoi, and Tanjong Kling).

Table 4-14. PUB's Categorization of Used Water Dischargers.

Source: Courtesy of PUB.

Group	Category	Basis	Type of Business (Example)
High Risk	Cat. 1	Dischargers with: a. potential to impact WRPs' operation or NEWater production or pose health & safety hazard to workers maintaining public sewerage system, or b. three or more offences	Toxic waste collectors, pharmaceutical companies, wafer fabs, electroplating companies and printing companies
	Cat. 2	Dischargers with two or less offences	Metal finishing, machine/equipment repair & servicing, shipyard, aerospace, and wafer production support companies.
Low Risk	-	Unlikely to affect WRPs' operation or NEWater production or pose health & safety hazard to workers maintaining public sewerage system and/or no offence	Food factory, laboratory, laundry, assembly & testing, bio-medical, construction sites, warehouse, and logistics companies

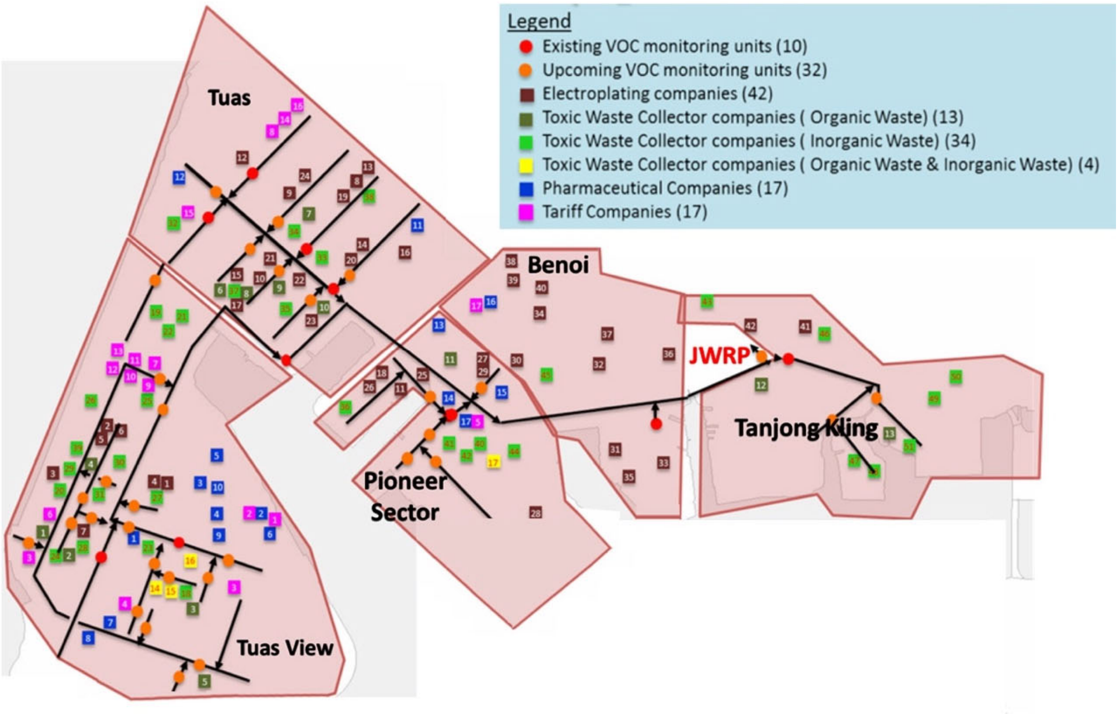


Figure 4-11. Distribution of Industrial Dischargers in the JWRP Catchment Area and Location of VOC Monitoring Units.
Source: Courtesy of PUB.

The VOC monitoring units were deployed between November 2011 and November 2012. Figure 4-12 shows a clear decrease in the number of high VOC incidents (e.g., >50 mg/L) in the JWRP catchment since the VOC monitoring units were installed. PUB has also confirmed that a reduction in the concentration of toluene and methylene chloride in the influent water has been attributed to the reduction of VOC-related incidents at JWRP.

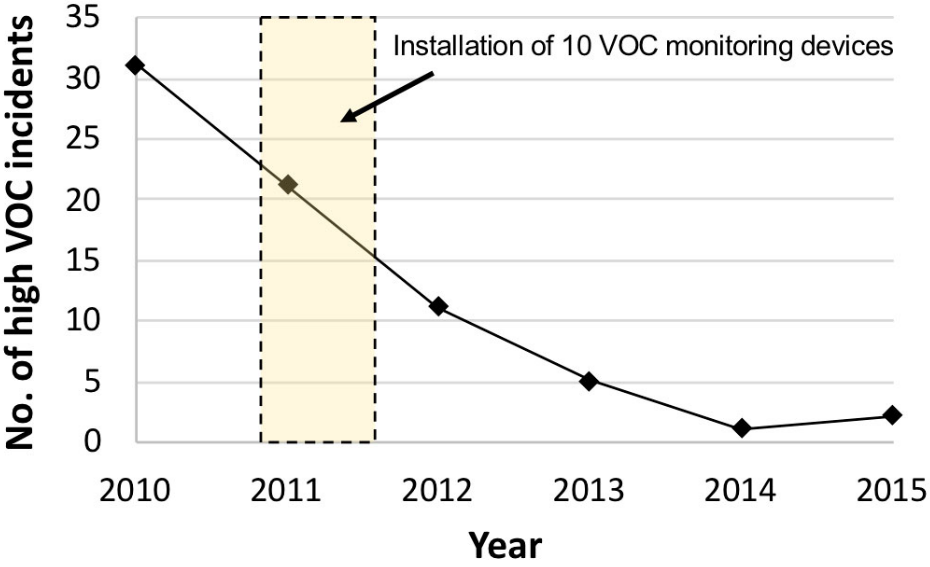
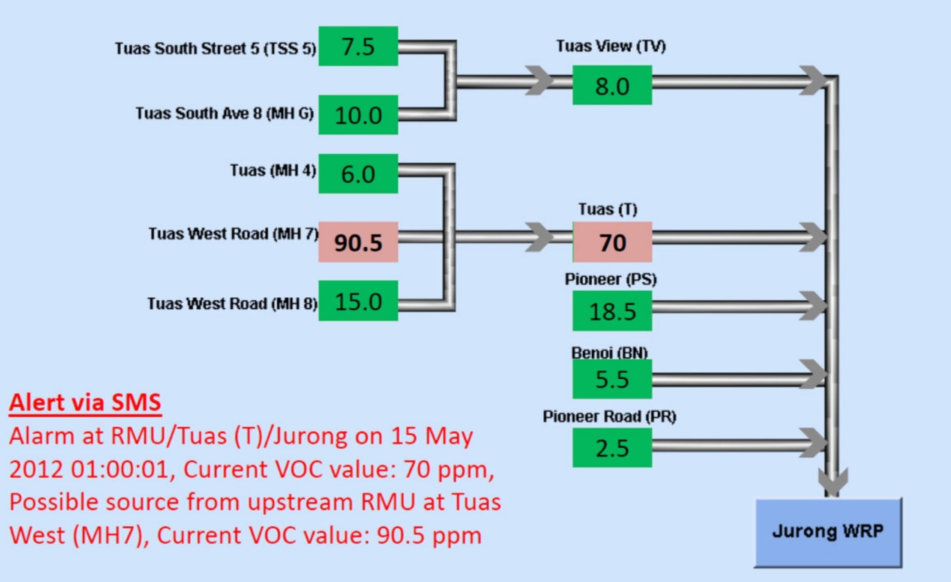


Figure 4-12. High VOC Incidents at JWRP between 2010 and 2015 Relative to Installation of VOC Monitoring Devices.
Source: Courtesy of PUB.

Figure 4-13 illustrates an example of how the VOC monitoring units at JWRP are employed to capture a high VOC incident. During this event (May 15, 2012), an alarm was triggered for the Tuas (T) monitoring unit with a VOC value of 70 mg/L. The source water to this unit comes from three locations: Tuas (MH 4), Tuas West Road (MH 7), and Tuas West Road (MH 8). Only Tuas West Road (MH 7) was reading abnormally, at 90.5 mg/L. By receiving alerts from these locations, PUB can react more quickly to sudden changes in VOCs across their network. In their first year of operation (2011-2012), PUB received 20 alerts of high VOC incidents. In 18 of these cases, PUB was able to identify the source that discharged the chemicals into the public sewers.



Alert via SMS

Alarm at RMU/Tuas (T)/Jurong on 15 May 2012 01:00:01, Current VOC value: 70 ppm, Possible source from upstream RMU at Tuas West (MH7), Current VOC value: 90.5 ppm

Figure 4-13. VOC Monitoring Units during a High VOC Incident at JWRP Catchment Area.

Source: Courtesy of PUB.

4.3.4.2 Documented Illicit Chemical Discharges at Kranji NEWater Facility

The Kranji NEWater facility (KNF) is located in northern Singapore and produces high-grade reclaimed water for both industrial and indirect potable reuse purposes. The facility is comprised of three main phases. Initially commissioned in 2003, the current plant capacity is 22 MGD. The treatment process train in the NEWater plant consists of microfiltration (MF), RO, and ultraviolet disinfection (UV). The KNF has strict operating bounds with limits often more conservative than industrial customer specifications. Table 4-15 provides a summary of customer specifications, action and shutdown levels for key water quality parameters.

The NEWater action and shutdown TOC limits were established based on an extensive set of NEWater quality data collected during the NEWater demonstration phase between 2001 to 2002, as well as many consultations with stakeholder industries, such as wafer fabrication plants, to confirm that the TOC levels were acceptable for wafer fabrication processes and other customer needs.

Table 4-15. KNF RO Operating Control Limits for Key Parameters.

Source: Courtesy of PUB.

Process	Parameter	Customer Specification	Action Limit	Shutdown Limit
RO Permeate	TOC[1]	< 500 µg/L	> 80 µg/L or; three consecutive readings show increasing TOC levels > 10 µg/L per reading, or; baseline shift > 10 µg/L with continuous uptrend	> 150 µg/L
	Conductivity	< 150 µS/cm	> 50 µS/cm	> 150 µS/cm

1 – response plan when RO permeate TOC exceeds the action limit is to recycle RO Stage 2 permeate to MF/UF filtrate tank

When a parameter exceeds action limits but is within shutdown limits:

1. Staff immediately investigates to bring parameter reading within control limit
2. If deviation cannot be returned to operating range within 60 minutes, staff seeks advice from Plant Manager on whether to continue treatment / supply or stop treatment / supply. Plant Manager shall obtain approval from Division Head to continue treatment while monitoring the water quality trend.

When a parameter exceeds shutdown limits:

1. Staff must stop treatment and supply and rectify the faults.
2. If Shutdown limits are breached due to sudden spike/dip, 15 mins is allowed for water quality to normalize. Otherwise, staff is to stop treatment / supply and rectify the faults.

4.3.4.3 May 2017 Kranji NEWater Facility High TOC incident

On May 17, 2017, the KNF experienced a high TOC incident that was ultimately found to be caused by the presence of *N,N*-dimethylacetamide (DMAc) in the RO permeate.

On this day, the RO permeate TOC baseline at KNF prior to the incident was 45-53 µg/L and 30-40 µg/L for Phase 1 and Phase 2, respectively[10]. RO permeate TOC trending during this day is shown in Figure 4-14. By 9:30 AM, the TOC readings were 55 µg/L and 40 µg/L for Phase 1 and Phase 2, respectively. Based on a baseline shift of > 10 µg/L and a continuous uptrend for both monitoring locations, action limits were triggered per Table 4-15 and samples were collected for GC-MS testing. By 9:45 AM, elevated TOC readings persisted (i.e., 60 µg/L for Phase 1 and 45 µg/L for Phase 2), such that a plant shutdown was triggered. Upon shutdown, KNF continued to pump to its network from its product water tanks serving as a buffer during the disruption of NEWater production. Between 9:45 AM and 2:00 PM, KNF was completely flushed and subsequently re-started using potable water as source water. At 4:00PM, a blend of KWRP secondary effluent and potable water was used as KNF source water. At 5:30 PM, KWRP secondary effluent alone was used as KNF source water and KNF was operated at full output.

Samples were collected during this high TOC event for investigative purposes. GC-MS samples identified that the cause of the incident was presence of DMAc. The DMAc GC-MS results during this event are shown in Table 4-16. DMAc is used by wafer fabricators for wafer cleaning. PUB has followed up accordingly with the discharger involved.

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[10] Phase 1 and Phase 2 refer to different banks of RO trains that are monitored independently

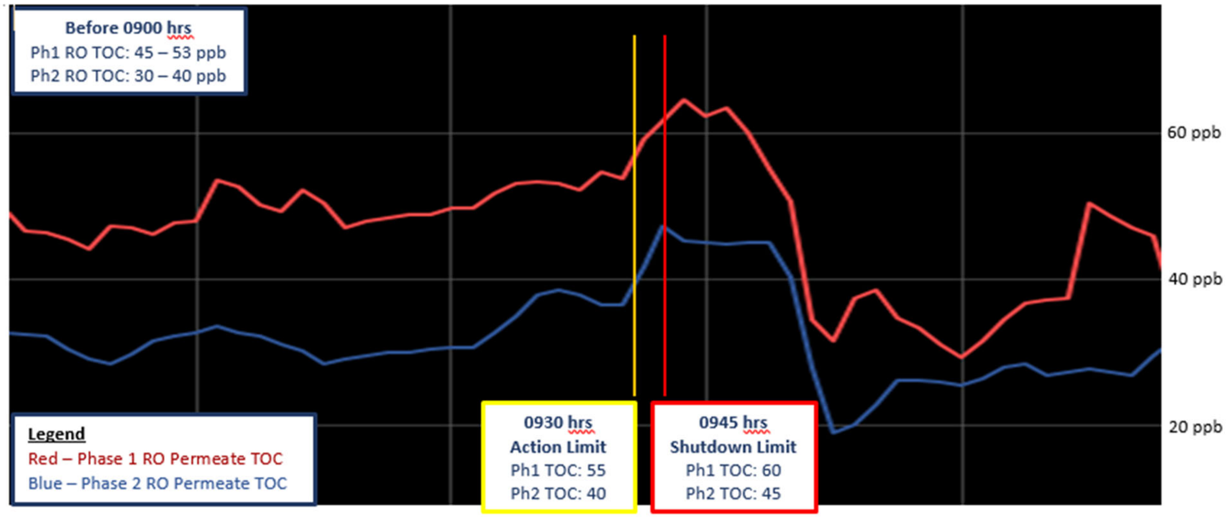


Figure 4-14. VOC Monitoring Units during a High VOC Incident at JWRP Catchment Area.
Source: Courtesy of PUB.

Table 4-16. DMAc GC-MS Results during High TOC Event.
Source: Courtesy of PUB.

Sample Collection Time- Date	*N,N*-dimethylacetamide (DMAc)		
	KWRP Secondary Effluent	**MF Feed**	**RO Permeate**
9:30 AM – May 10th	ND*	9.39 µg/L	4.77 µg/L
2:30 PM – May 10th	12.4 µg/L	*not sampled*	*not sampled*
6:30 PM – May 10th	3.35 µg/L		
10:30 PM – May 10th	ND		
2:30 AM – May 11th	ND		
6:30 AM – May 11th	ND		

* DMAc peak might have been masked from effluent TOC

4.3.4.4 February 2019 Kranji NEWater Facility High TOC incident

On February 12, 2019, KNF had a high TOC event where acetone was identified as a cause. Based on lab sampling results, acetone (~270 ppb) and methyl isobutyl ketone (~25 ppb) were detected in the RO permeate samples on this day. Preliminary investigation indicated that the high TOC was caused by a company in the wafer cleaning industry. PUB followed up accordingly with the company involved.

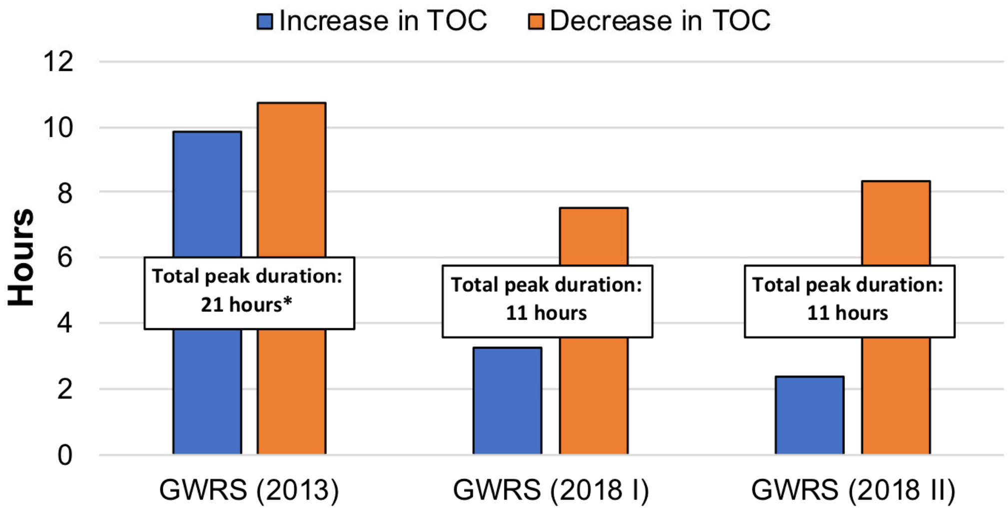
4.3.5 Common Features of Documented Chemical Peaks

Among the three utilities evaluated, it was identified that neutral low molecular weight compounds were the cause for the chemical peaks observed. Acetone, in particular, was identified as the cause for chemical peaks across all three utilities. Acetone is the simplest and smallest ketone with a molecular weight of 58.08 g/mol.

One common feature of the documented chemical peaks was they appeared to *tail-off* more slowly than when on the rise to peak value. Figure 4-15 captures the duration of RO permeate TOC increase and decrease for select case study chemical peaks, where the total peak duration is the sum of the increase and decrease times. This is characteristic of a mixed tank rather than a plug-flow reactor and may be attributed to the fact that dispersion occurs between discharge location (i.e., sewershed) and monitoring location (i.e., RO permeate). In addition, it is possible that some illicit charges may occur in step-feed manner (as a continuous discharge over a certain period), rather than as an instantaneous discharge (a pulse). In this case, the chemical peak width would further increase and be subject to additional dispersion between the sewershed and AWPF.

In summary, the chemical peaks evaluated from the case study utilities had the following characteristics:

1. Chemical peaks were caused by passage of neutral low molecular weight compounds
2. TOC monitoring was effective for identifying the presence of neutral low molecular weight compounds in the RO permeate which caused the peaks. RO feed TOC analyzers were not as effective in capturing chemical peaks during low concentration peak events – likely due to *masking* and/or diurnality of the ambient feed TOC.
3. Chemical peaks lasted on the order of several hours to days
4. Peak TOC values were not instantaneously achieved during chemical peak events, suggesting dispersion and/or mixing of the discharged chemical or that the chemical was discharged in a *step-feed* (continuous) manner
5. The decrease in TOC took longer than the increase in TOC during chemical peak events, suggesting that the reduction of chemical peaks takes longer than their increase to the peak value.



**only accounts for large peak which began 2/18/2013 8AM*

Figure 4-15. Duration of TOC Increases and Decreases for Select Case Study Chemical Peaks.

CHAPTER 5

Chemical Peaks in DPR Scenarios

In order for a chemical peak to occur, an abnormal event (i.e., illicit discharge) must take place. This chapter explores the impacts of variables surrounding the illicit discharge on chemical peak characteristics when the peak reaches the treatment facility and throughout treatment. Downstream of the AWTF, the amount of blending water available and mode of DPR (SWA, TDWA, etc.) significantly impacts the balance of source control, monitoring, treatment, and blending required to successfully "average" chemical peaks.

5.1 Variables Impacting Chemical Peak Characteristics

This section discusses the key influences on chemical peak characteristics relevant to utilities practicing direct potable reuse. The following variables are discussed:

1. Sewershed size
2. Discharge volume
3. Discharge location
4. Discharge duration
5. Treatment robustness
6. Blending

5.1.1 Impact of Sewershed Size

A sewershed can be described as a receiving body for sewers that flow to a single point, typically a WWTP. If an illicit chemical discharge were to occur, at least a portion of the sewershed would be contaminated from the discharge. As such, the size of the sewershed plays a role in "averaging" (i.e., dampening and diluting) a chemical peak since the sewershed can offer dilution and possible dispersion in the event of an illicit chemical discharge[11].

For theoretical evaluation in this study, the size of a sewershed can be understood as the receiving WWTP flow capacity. For example, a WWTP with 100 MGD capacity has a sewershed size of 100 MG. In contrast, a WWTP with 10 MGD capacity has a sewershed size of 10 MG. If the same chemical discharge (in terms of mass) were to occur for either sewershed, the smaller one would have a resulting chemical concentration 10-fold higher than the larger sewershed[12]. As such, it can be said that smaller sewersheds are more vulnerable to illicit chemical discharges than larger sewersheds and thus inherently demand tighter source control monitoring and deterrence. In some instances (and if possible), a small sewershed would benefit from treating industrial and domestic sewerage separately.

Figure 5-1 illustrates a scenario where a tanker truck containing approximately 4,500 gallons of acetone is illicitly discharged into two sewershed sizes (10 MG and 100 MG). Based on acetone's carbon content and specific gravity, this discharge would result in a TOC increase of 220 mg/L and 22 mg/L in the WWTP influent for a sewershed size of 10 MG and 100 MG, respectively. Such levels of acetone are not

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[11] It is understood that sewersheds do not offer ideal plug flow reactor conditions. As such, there is dispersion within a sewershed.

[12] This example does not account for dispersion for simplicity. It is expected that dispersion would occur in the sewershed and inherently benefit the averaging of a chemical peak.

considered toxic to activated sludge, yet it is likely that more passage of acetone through the WWTP would occur for the 10 MG sewershed size scenario, such that final product from a supplying AWPF would be more severely impacted.

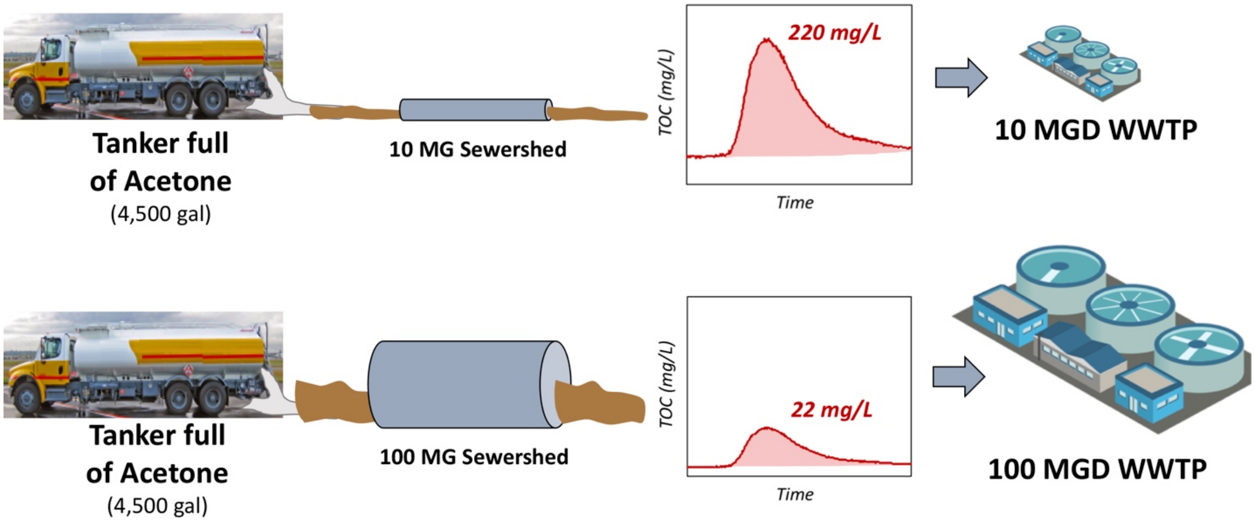

Figure 5-1. Impact of Sewershed Size for a Theoretical Illicit Chemical Discharge.

5.1.2 Impact of Discharge Volume

The volume of chemical discharged to a sewershed will have a direct impact on the magnitude of a chemical peak and effects on downstream processes (i.e., WWTP and AWPF). The greater the volume of chemical discharged, the larger the magnitude of the peak and effect on downstream processes. A theoretical example is illustrated in Figure 5-2, where a discharge from a tanker truck full of acetone (i.e., 4,500 gal) is compared to a discharge of a 55-gal drum and a 1-gal bottle for a sewershed of equal size. The tanker discharge would result in a TOC concentration of 220 mg/L, whereas the 55-gal drum would lead to a TOC concentration of 3 mg/L and 1-gal bottle would only contribute 0.1 mg/L TOC in the WWTP influent given a 10-MG sewershed. This compares to a typical range for untreated wastewater TOC concentration of 109-328 mg/L (Tchobanoglous et al. 2015). Thus, high volume dischargers (e.g., industrial dischargers) are those that pose the greatest risk on the magnitude of chemical peaks.

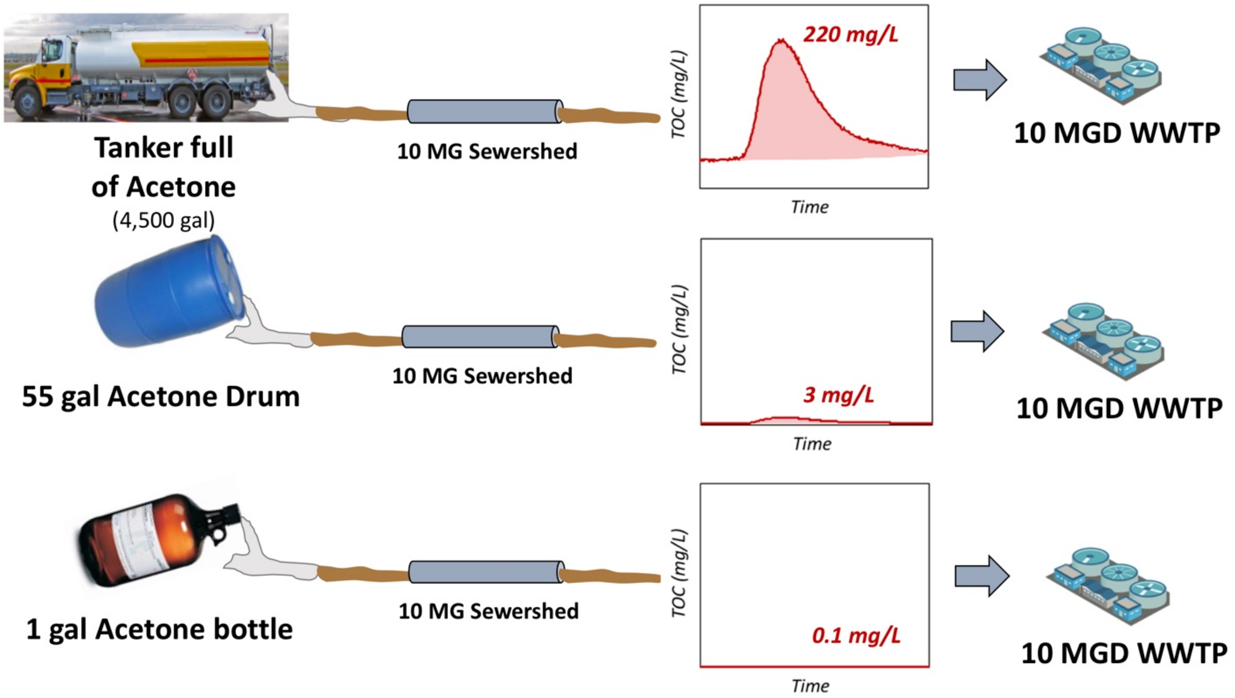

Figure 5-2. Impact of Discharge Volume for a Theoretical Illicit Chemical Discharge.

5.1.3 Impact of Discharge Location

The location of discharge within a sewershed network can have an influence on the magnitude and shape of a chemical peak. This concept is supported by inherent dispersion that occurs throughout the sewershed network. In terms of a chemical peak, the opportunity for dispersion increases as the discharge location moves away from the receiving WWTP. A utility benefits from sewershed dispersion since a peak will be distributed over a longer period of time, lowering the maximum concentration observed. In other words, dispersion dampens the height – i.e., peak concentration – of the peak. Longer peak duration also provides the opportunity for subsequent abatement across the WWTP or AWPF to de minimis levels.

A discharge occurring far away from the receiving WWTP is also more likely to be captured through any sewershed monitoring, providing increased response time to handle chemical peaks.

A discharge occurring near or at the head of the WWTP would have a much higher peak maximum value, such that even after the WWTP and AWPF, chemical peak levels may persist at concentrations that are of concern and require further action, such as a diversion or additional treatment. This type of discharge would also have a much shorter duration. Overall, even though peak "averaging" occurs with dispersion, the total mass loading remains the same.

Figure 5-3 illustrates the effect of discharge location within a sewershed of equal size when subjected to an illicit discharge of one tanker truck full of acetone (i.e., 4,500 gal). Although the total mass under a peak will be the same for either scenario, the magnitude (height/concentration) of the peak is far greater when the discharge occurs in the vicinity of the WWTP. A discharge occurring far from the WWTP has the opportunity to disperse which causes averaging of the peak. As such, it can be said that discharges occurring in the vicinity of a WWTP are the most critical as the magnitude of peak will be the greatest. Source control programs could consider prioritizing the monitoring and compliance of industrial facilities closer to the WWTP.

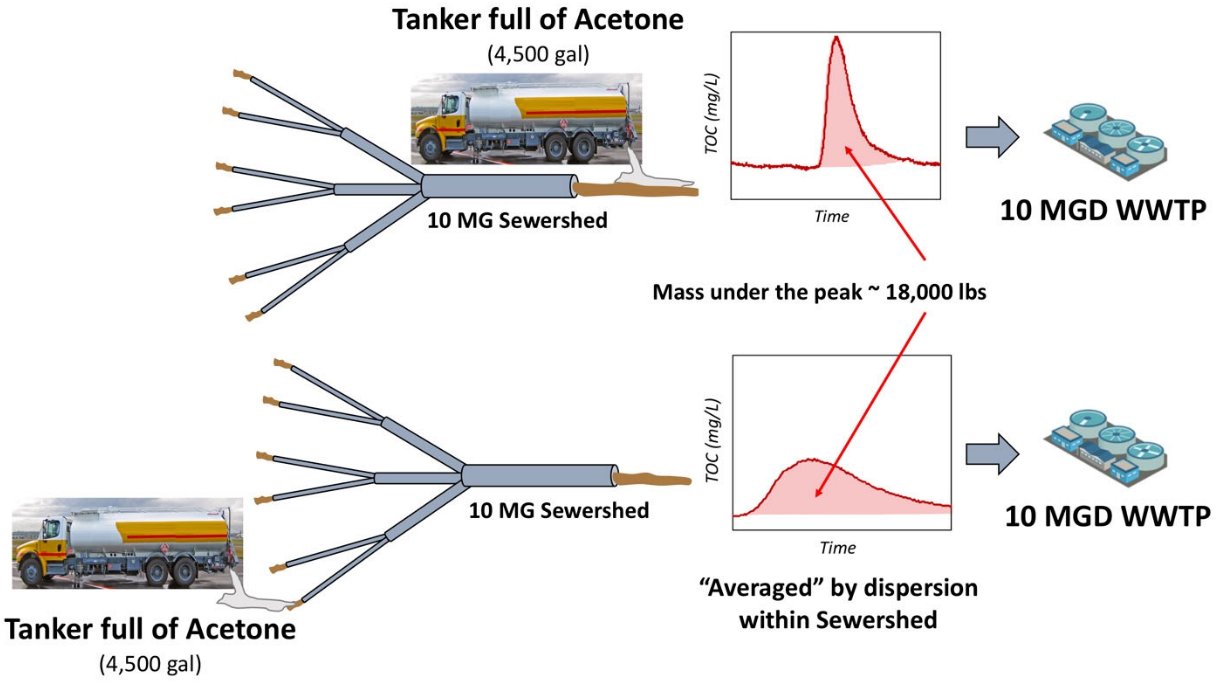

Figure 5-3. Impact of Discharge Location for a Theoretical Illicit Chemical Discharge.

5.1.4 Impact of Discharge Duration

Considering an equal mass chemical discharge, the duration of the discharge will directly impact the shape of a peak. This occurs since there is greater dilution of a chemical as discharge duration increases for the same mass discharge. Consider one tanker truck full of acetone (i.e., 4,500 gal) that is discharged to a 0.2 MG[13] sewershed in less than one hour versus one day (24 hours). Although the total mass discharged is the same, the one-hour discharge will result in greater peak concentration than for the one day scenario. Figure 5-4 illustrates this scenario, where the resulting maximum TOC value for a less than one-hour discharge would be 9,430 mg/L compared to 448 mg/L for a one-day discharge of one tanker truck full of acetone. The TOC values assume the sewershed is an ideal CSTR condition. As such, short-duration illicit chemical discharges are the most critical to AWPF final product water quality.

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[13] The sewershed size was chosen based on proportion to that of OC San. Considering CSTR conditions for the sewershed, the size of sewershed also impacts the magnitude of the peak (i.e., larger sewersheds offer more dilution of the peak). A smaller sewershed will approximate conditions of plug-flow reactor, resulting in higher peak concentrations, such that short duration discharges are most critical.

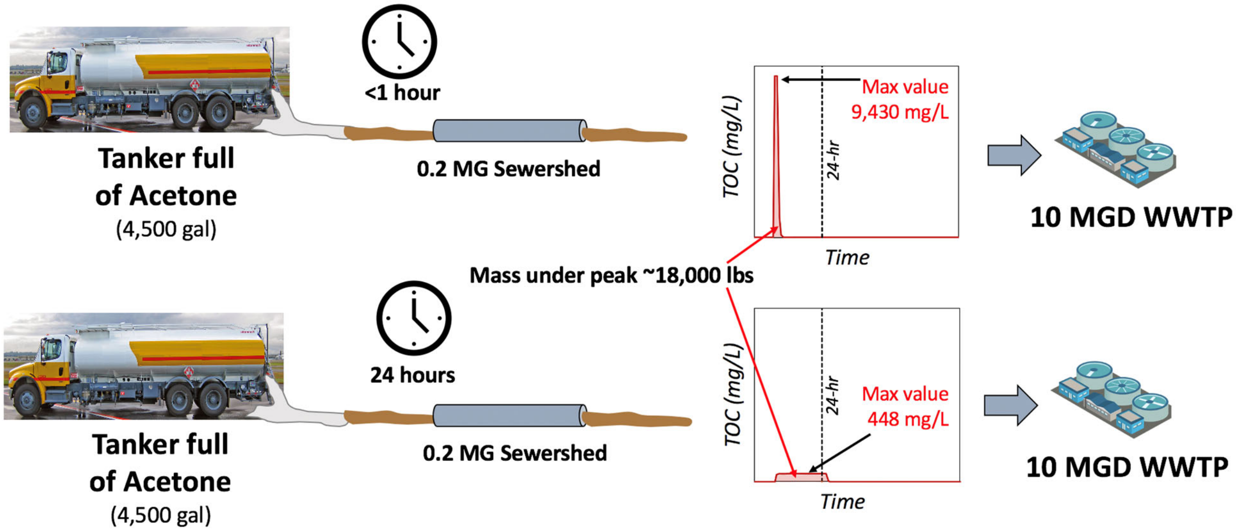

Figure 5-4. Impact of Discharge Duration for a Theoretical Illicit Chemical Discharge.

5.1.5 Impact of Treatment Robustness

Treatment robustness is the ability of a potable reuse system to address a broad variety of contaminants and resist catastrophic failures (Pecson et al. 2015). In terms of chemical peaks, a robust treatment train is beneficial in that it can help abate the passage of compounds that would otherwise pass through. This is achievable by adding processes that offer a spectrum of treatment mechanisms, including biodegradation, adsorption, photolysis, oxidation, and physical separation.

As captured during the challenge test at City of San Diego's 1 MGD demonstration, the use of O_3/BAC as pretreatment to FAT provided further abatement of the spiked compounds (i.e., NDMA, formaldehyde, 1,4-dioxane, acetone). To illustrate the impact of treatment robustness on chemical peaks, a theoretical scenario using compound removal data from the challenge test studies is captured in Figure 5-5[14]. For this example, a discharge containing 25 lbs of acetone, formaldehyde, NDMA, and 1,4-dioxane (i.e., 100 lbs total) is subjected to a treatment train with O_3/BAC pretreatment to FAT and FAT alone. The resulting TOC and total mass load in the product water are significantly lower when O_3/BAC was added as pretreatment as a result of increased robustness – particularly on formaldehyde and acetone removal. Product water TOC was 0.6 mg/L with O_3/BAC pretreatment and 2.4 mg/L without O_3/BAC pretreatment (feed water TOC: 5.1 mg/L). As such, a robust treatment train can dampen peaks to provide peak "averaging."

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[14] Removal achieved during challenge tests were site-specific and are not to be considered universal. Site-specific factors such as source water quality and BAC age/performance can affect ability of treatment trains to address peaks.

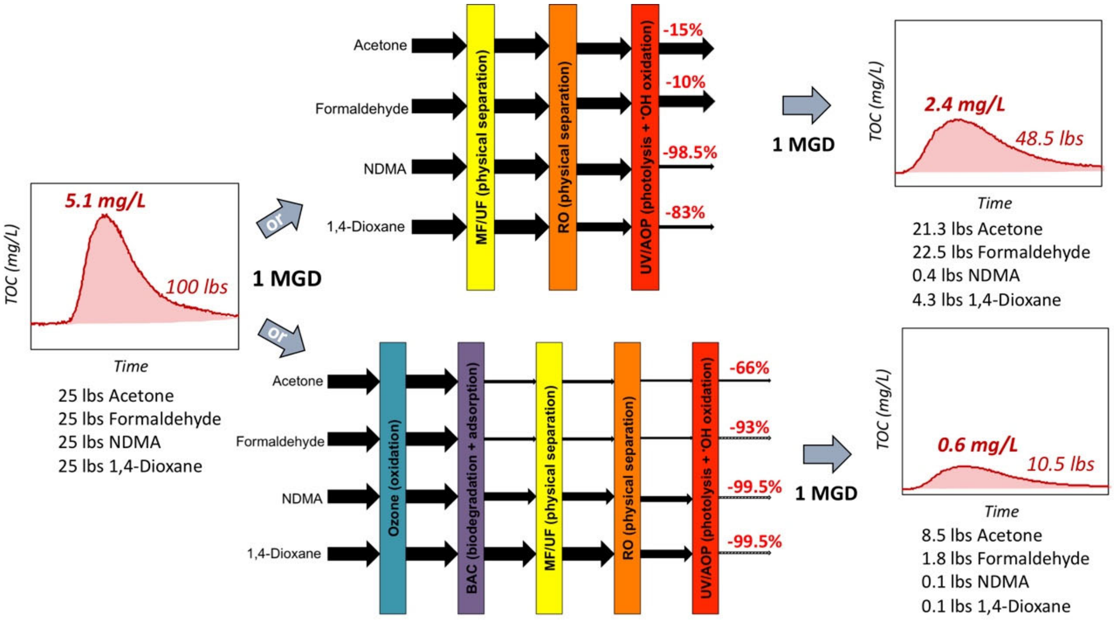

Figure 5-5. Conceptual Fate of Spiked Compounds When Subjected to Different Treatment Trains.

5.1.6 Impact of Blending

Blending can offer “averaging” of chemical peaks if there is sufficient retention time in the blending system (e.g., tank, reservoir) to partially dilute a peak. Related to DPR applications, blending can be achieved by the addition of an engineered buffer or a “small reservoir” that does not meet SWA requirements for dilution and therefore is not defined as SWA (surface water augmentation) in the California water recycling regulations.

In order to quantitively evaluate the impact of blending on chemical peaks, a continuously stirred tank reactor (CSTR) model was developed to evaluate the effluent concentration for various retention time scenarios. The model assumed CSTR conditions for simplicity. The CSTR model input represents the TOC concentration of finished water from an AWPF that is entering a theoretical blending system (tank or reservoir). The 2013 GWRS acetone event (discussed earlier) was used as the input to the model, since it was seen as the worst case scenario observed in terms of chemical peaks for potable reuse applications. Based on the 2013 GWRS peak characteristics, two 10 hour-steps were used as inputs to the model. The first 10-hour step was set to have a concentration of 0.9 mg/L, whereas the second 10-hour step was set to have a concentration of 5.7 mg/L. The 2013 GWRS RO permeate TOC data with the two 10-hr peaks overlaid is shown in Figure 5-6. The reasoning behind separating these two steps was to approximate the characteristics of the 2013 GWRS peak and to use a similar total mass load discharged during the event. As for modeling scenarios, two sets of conditions were evaluated. The first condition considered the impacts of blending for tanks (i.e., engineered buffers) with a residence time of 3, 6, 12, and 24 hours. Figure 5-7 shows the resulting effluent TOC over time as a function of the different residence time tanks. Maximum theoretical TOC observed for the tanks was 5.5 mg/L for the 3-hour tank, 4.7 mg/L for the 6-hour tank, 3.4 mg/L for the 12-hour tank, and 2.2 mg/L for the 24-hour tank. The second condition considers the impact of blending using reservoirs with a residence time of 1, 10, 30, and 60 days. Figure 5-8 shows the resulting effluent TOC over time as a function of the different retention time reservoirs. Maximum theoretical TOC observed for the reservoirs was 0.05 mg/L for the 60-day reservoir, 0.1 mg/L for the 30-day reservoir, 0.3 mg/L for the 10-day reservoir and 2.2 mg/L for the 1-day reservoir. The resulting TOC in the reservoir is solely from the modeled chemical peak (i.e., the reservoir is assumed to have 0 mg/L TOC initially).

The model revealed that the degree of peak "averaging" (dampening) in the product water exiting the blending system (tank or reservoir) was increased with residence time. That said, the total mass load was not affected by residence time; rather, the same mass is distributed over longer time periods when retention time increased. The modeled tank scenarios only offered modest peak dilution. A tank with a retention time of 3 hours was not particularly effective in terms of peak averaging, since the maximum concentration observed was 5.5 mg/L during the 5.7 mg/L input. A retention time of 24 hours offered a reduction of approximately 60% in terms of the maximum concentration observed (i.e., 2.2 mg/L) relative to the step input of 5.7 mg/L. As for the modeled reservoirs, a retention time of 10 days was sufficient to "average" the maximum concentration from 5.7 mg/L to 0.30 mg/L. In other words, a 10-day reservoir with ideal CSTR characteristics would be sufficient to dampen this worst case-scenario observed chemical peak to levels below those permissible per current indirect potable reuse for groundwater replenishment (i.e., TOC of 0.50 mg/L)[15].

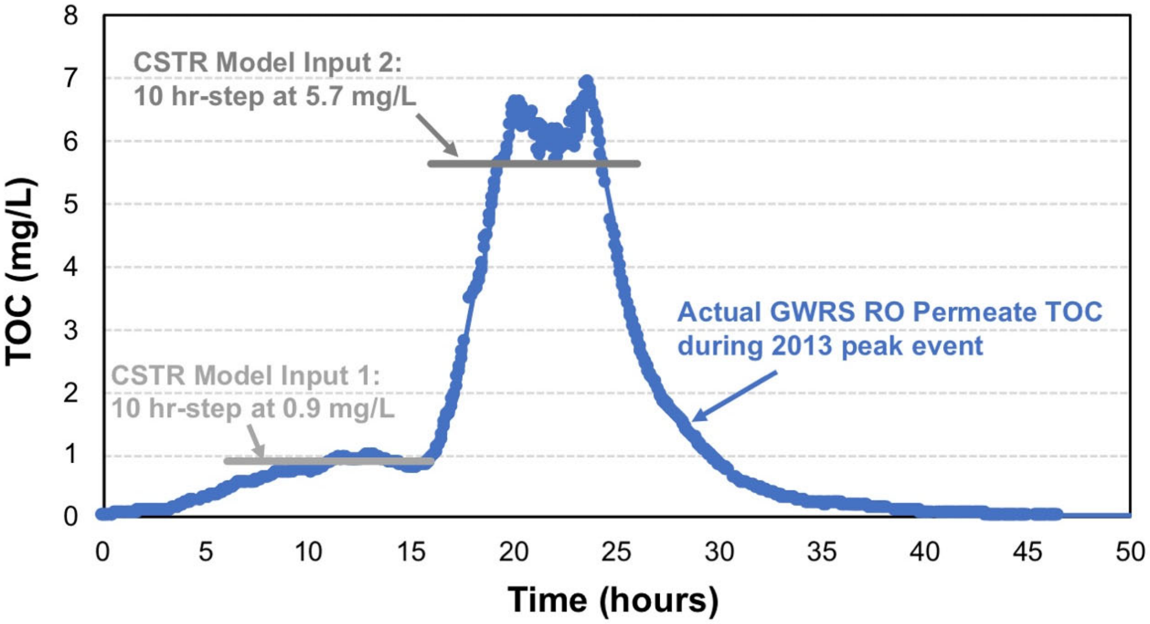

Figure 5-6. GWRS 2013 RO Permeate TOC Peak Data (Blue) with Model Step Inputs Overlaid (Grey).

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[15] A product water TOC concentration of 0.30 mg/L may be enough to trigger a response (e.g., investigation). Facilities have site-specific response level TOC concentrations, such as that shown in Table 4-11 for GWRS.

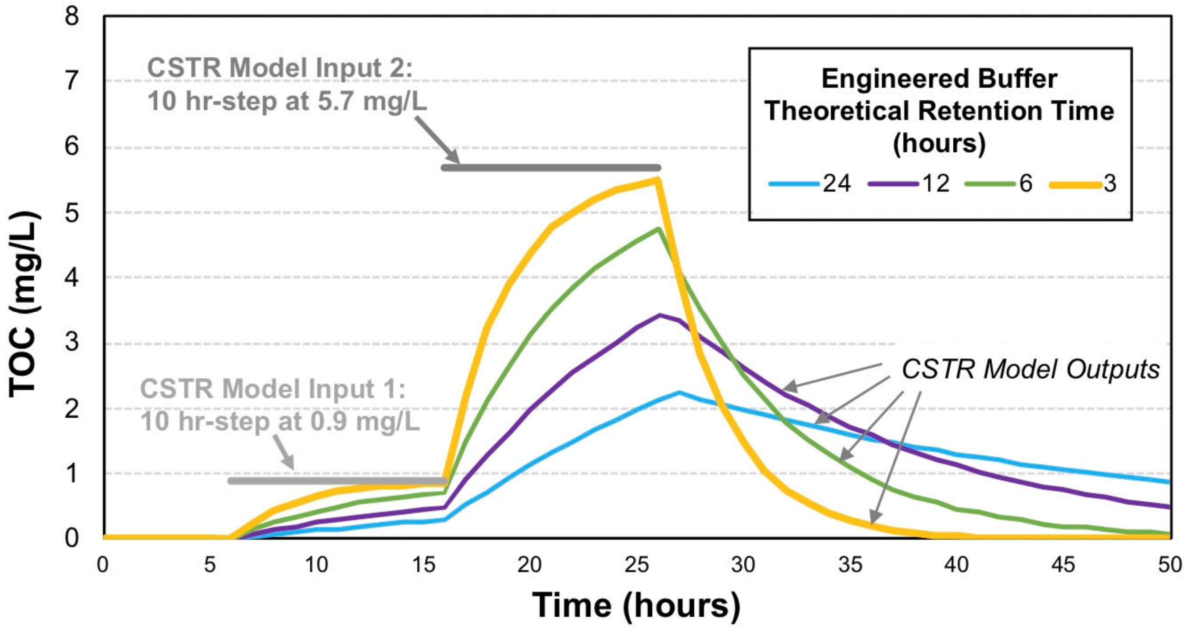

Figure 5-7. Blended TOC of Varying Residence Time Tanks (CSTR) When Subjected to Tank Feed Water Quality (Grey Line) That Exhibits a Chemical TOC Peak Similar in Size and Duration to the 2013 GWRS Acetone Event.

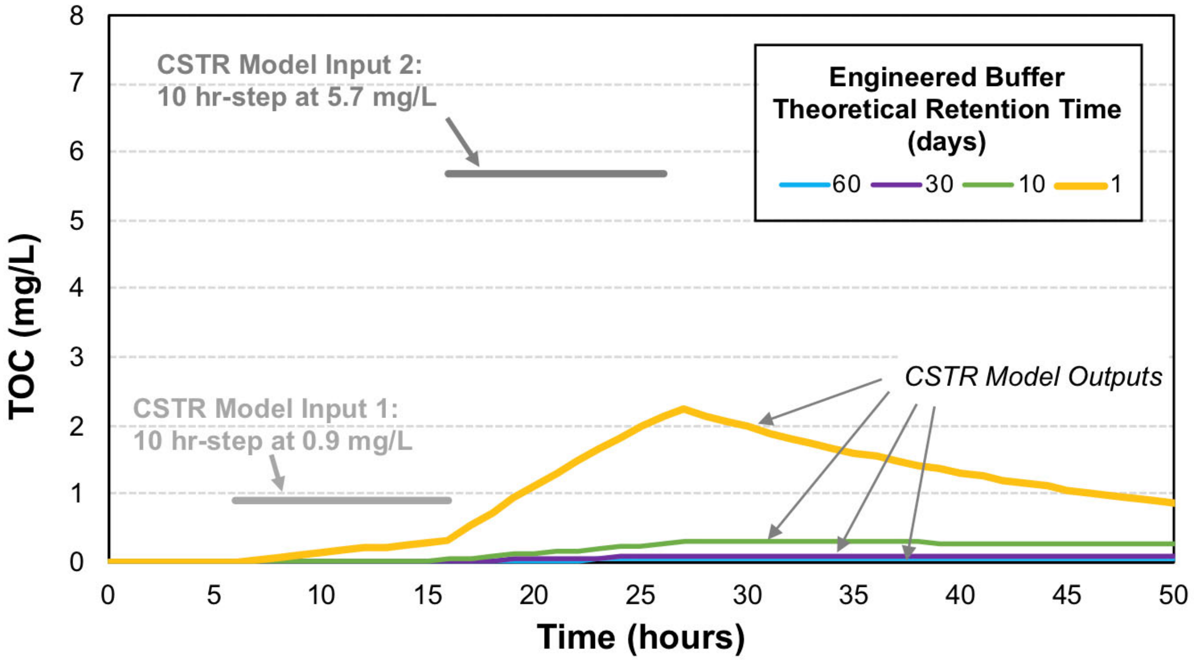

Figure 5-8. Blended TOC of Varying Residence Time Reservoirs (CSTR) When Subjected to Tank Feed Water Quality (Grey Line) That Exhibits a Chemical Peak Similar in Size and Duration to the 2013 GWRS Acetone Event.

5.2 Implications on Direct Potable Reuse Scenarios

The shift to DPR in the State of California can be characterized as the reduction (or elimination) of an environmental buffer between water purification and consumer distribution. An environmental buffer, consisting of a groundwater basin or a surface water reservoir, provides response time and in some cases an additional treatment barrier for a utility. Thus, the reduction or removal of that buffer requires greater control and assurance on the quality of advanced treated water. This section discusses the implications of chemical peaks for different DPR scenarios and how "averaging" of such peaks can be achieved. The following DPR scenarios are discussed:

1. Raw Water Augmentation with a "Small Reservoir"
2. Raw Water Augmentation with an Engineered Buffer (Tank)
3. Raw Water Augmentation without an Environmental or Engineered buffer
4. Treated Drinking Water Augmentation[16]

Figure 5-9 provides a schematic of these DPR scenarios in terms of location of WWTP, AWPF, environmental buffer (when used), and DWTP.

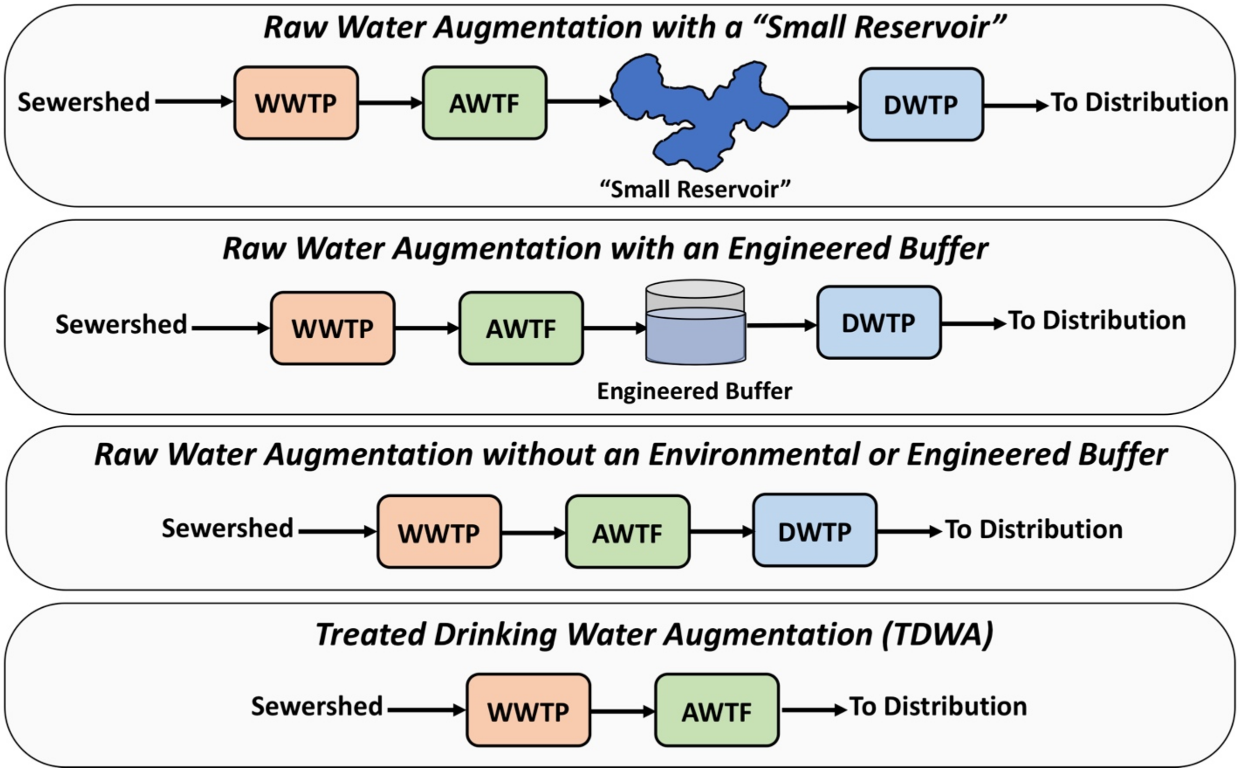

Figure 5-9. Schematic of DPR Scenarios.

5.2.1 Raw Water Augmentation with a "Small Reservoir"

Raw water augmentation with a "small reservoir" can be described as the supply of advanced treated water to a body of water that does not meet the storage nor dilution requirements to be considered indirect potable reuse (specifically, SWA). Per SWA regulations, an augmented reservoir must have a minimum theoretical retention time of at least two months and a minimum dilution of 100:1 (or 10:1 when subjected to additional disinfection treatment) determined by a validated hydraulic model as specified in the California Code of Regulations (22 CCR § 64668.30). The theoretical retention time is the value (in units of days) resulting from dividing the volume of water in the surface water reservoir at the

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[16] A Treated Drinking Water Augmentation followed by an engineered buffer can also be considered a DPR scenario. This can be compared to a drinking water storage tank (or reservoir) receiving water from a DWTP. Currently, these storage tanks are used to manage supply and demand. Only on rare occasions are these tanks (or reservoirs) kept full. Given that supply and demand is their main function, these forms of storage are not necessarily intended for chemical peak "averaging."

end of each month (V), by the total outflow from the surface water reservoir during the corresponding month (Q). Projects that do not meet theoretical retention time requirements are considered DPR, specifically Raw Water Augmentation (RWA). For the purpose of comparing DPR scenarios, a Raw Water Augmentation with a "small reservoir" would be the use of a reservoir that offers less than two months (60 days) theoretical retention time, wherein the theoretical retention time of a "small reservoir" is considered to be between 1 and 59 days.

For such a DPR scenario, the "averaging" of a chemical peak will occur from a combination of source control, treatment, monitoring, and blending. Treatment is achieved by the grouping of the WWTP, AWPF, and DWTP. Although the DWTP is mentioned, the WWTP and AWPF are considered the critical systems for chemical peak averaging since the DWTP is not designed for this purpose. The theoretical retention time offered by the "small reservoir" will directly correlate to the amount of blending that is achieved and thus chemical peak averaging. For this DPR scenario, the theoretical retention time of the "small reservoir" affects the relative weight of the other averaging components (i.e., source control, treatment, and monitoring) in any engineering design. A DPR project could still use a reservoir that doesn't classify as SWA per dilution requirements and still provide value in terms of chemical peak averaging, such that the necessity for further treatment can be lessened when compared to more direct forms of DPR (e.g., TDWA).

Figure 5-10 provides a hypothetical RWA scenario using a "small reservoir" with 30 days of theoretical retention time. This "small reservoir" is expected to offer a large degree of peak "averaging" through blending (refer to Figure 5-8). As such, the fate of a chemical peak is "averaged" mostly through blending in the DPR scenario. In scenarios where sufficient theoretical retention time is available to achieve blending effects (e.g., >10 days of theoretical retention time), the use of additional treatment, source control, and monitoring would make a DPR application more redundant, but not necessarily more capable in terms of averaging chemical peaks to a level that is below concern. As such, blending from a "small reservoir" could be part of averaging a chemical peak and should be considered as an important component as part of DPR implementation.

Another way to illustrate the ability of "small" reservoirs to "average" chemical peaks is by plotting the theoretical dilution of different sizes of reservoirs considering chemical peaks of different durations under CSTR conditions. This relationship is shown in Figure 5-11. The degree of peak averaging is a function of (a) the size (V/Q) of the buffer and (b) the duration of the off-spec pulse of water entering the buffer. As the off-spec pulse continues to enter the buffer, that off-spec water becomes an increasingly larger percentage of the water in the buffer leading to lower and lower degrees of dilution.

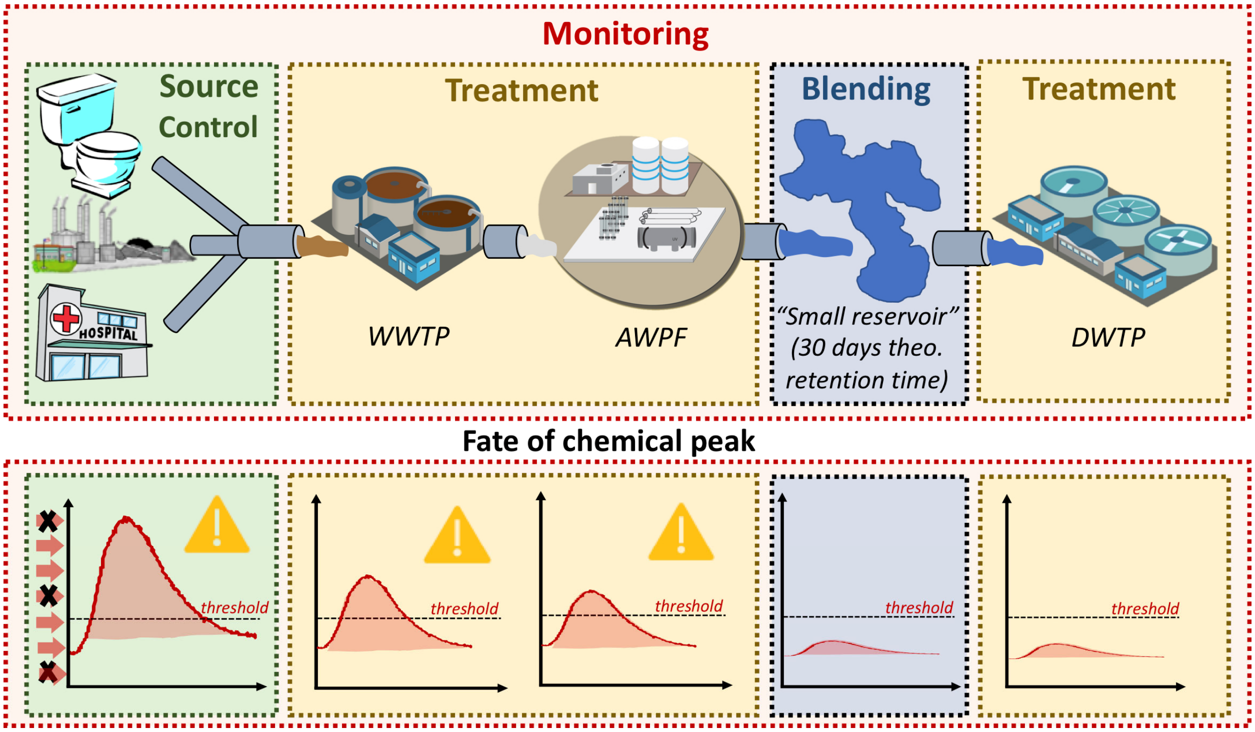

Figure 5-10. Hypothetical Fate of a Chemical Peak for a Raw Water Augmentation DPR Scenario Using a "Small Reservoir" with 30 Days of Theoretical Retention Time.

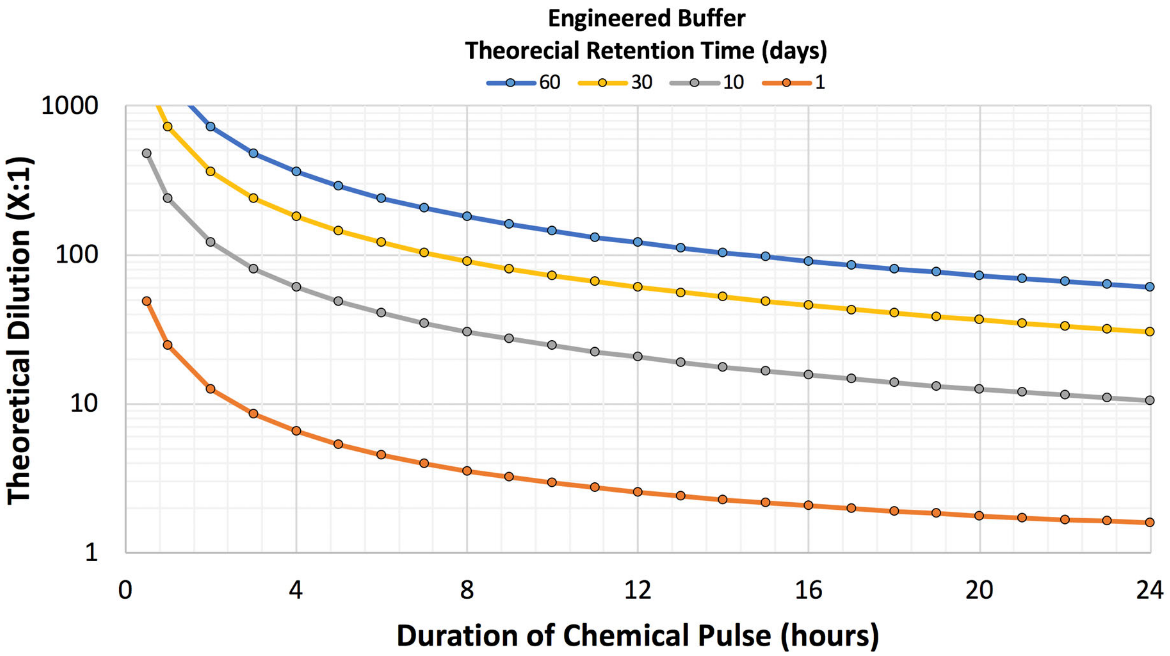

Figure 5-11. Dilution Provided by Buffers of Various Sizes Is Impacted by Both the Size of the Buffer and the Duration of the Failure.

Results assume that buffers behave as continuously stirred tank reactors.

5.2.2 Raw Water Augmentation with an Engineered Buffer (Tank)

The use of an engineered buffer (i.e., a tank) between the distribution of advanced treated water and supply to a DWTP has the goal of allowing sufficient time to measure and to be assured that the quality of water produced meets all applicable health standards (Leverenz and Tchobanoglous 2011). At only a fraction of the “small reservoir” in terms of theoretical retention time, an engineered buffer is not expected to offer significant chemical peak “averaging” through blending. However, it does provide response time in case a diversion (or shutdown) is preferable during a chemical peak event. In addition, redundant engineered buffers can be installed to isolate advanced treated water that may be of concern during peak events.

Figure 5-7 shows that there is limited peak “averaging” from engineered buffers sized for a theoretical retention time up to 12 hours. At 24 hours of theoretical retention time, peak averaging was limited to approximately 60% in terms of comparing the engineered buffer’s feed pulse concentration to its blended (effluent) concentration. It should be highlighted that a tank sized to offer 24 hours of theoretical retention time may not be feasible for certain application. For example, a facility with a flow capacity of 100 MGD would need to have a 100 MG sized tank to offer 24 hours of theoretical retention time, which is economically impractical. In this sense, additional averaging would need to instead be supplied by adding treatment, enhanced source control, and/or improved monitoring. Figure 5-12 depicts a source water augmentation scenario with a 12-hour theoretical retention time engineered buffer and shows the fate of a hypothetical chemical peak as a function of each component. For this scenario, the averaging of the peak is contributed primarily by source control, monitoring and treatment, since little peak averaging occurs for an engineered buffer of this size[17].

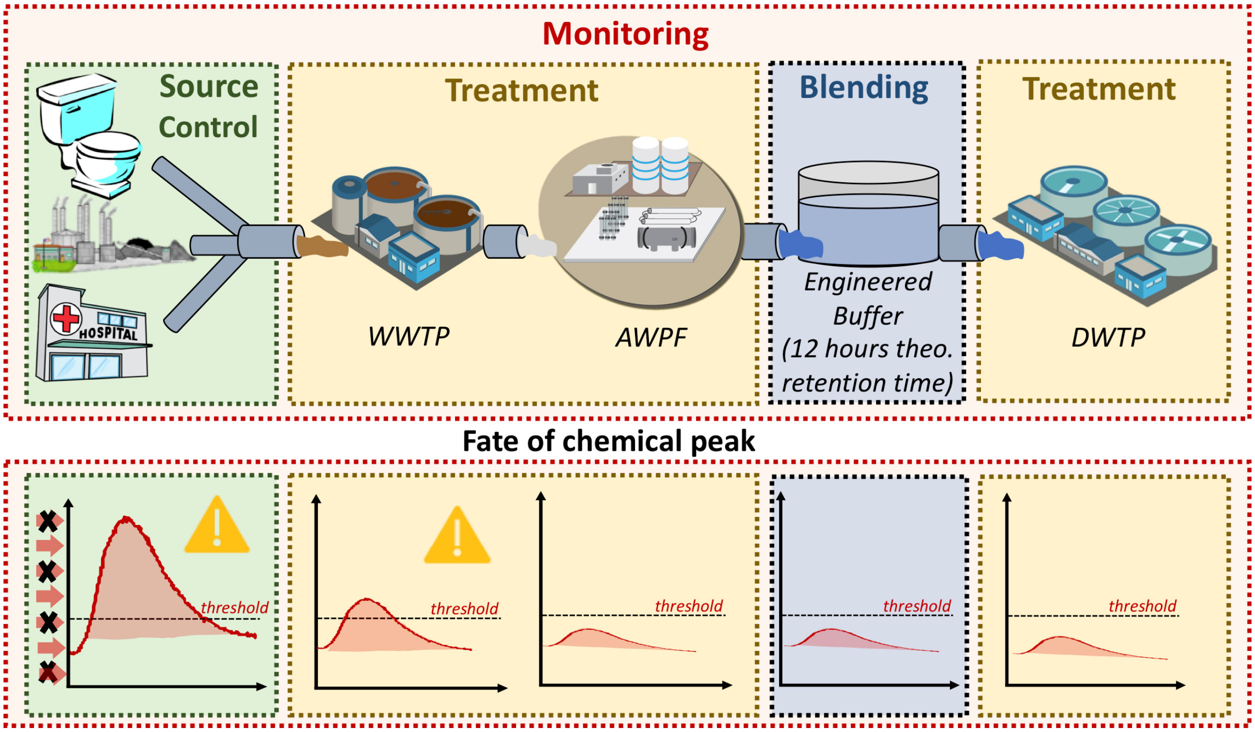

Figure 5-12. Hypothetical Fate of a Chemical Peak for a Raw Water Augmentation DPR Scenario Using an Engineered Buffer (Tank) with 12 Hours of Theoretical Retention Time.

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[17] Note, “averaging” from improved AWPF monitoring and enhanced source control monitoring occur in an indirect manner – through deterrence and prevention. A clear example of the effects of source control and monitoring on chemical peak averaging was observed when PUB installed multiple sewershed VOC monitors and saw a clear decrease in high VOC incidents thereafter (refer to Figure 4-12).

5.2.3 Raw Water Augmentation without an Environmental or Engineered Buffer

Raw water augmentation without an environmental or engineered buffer is a DPR scenario where advanced treated water is supplied directly to a downstream DWTP. As such, the need for enhanced source control, additional monitoring, and robust treatment are necessary to make up for the lack of a buffer that provides blending.

Figure 5-13 illustrates an RWA scenario showing the fate of a hypothetical chemical peak from sewer discharge to the supply of a downstream DWTP. For this scenario, the “averaging” of a chemical peak would occur solely from source control, monitoring, and treatment. Blending is not available for this scenario[18]. Robust treatment in this scenario is achieved by combining the WWTP, AWPF, and possibly additional processes targeted to abate compounds known to be challenging for removal through FAT. Although the DWTP is illustrated in the scenario and theoretically provides some degree of peak averaging, it is the WWTP and the AWPF that provide the majority of peak averaging. A utility considering RWA should not rely on a DWTP for chemical peak averaging as it is not designed to do so. In contrast, a robust and redundant AWPF treatment train should be considered to enhance chemical peak averaging ability.

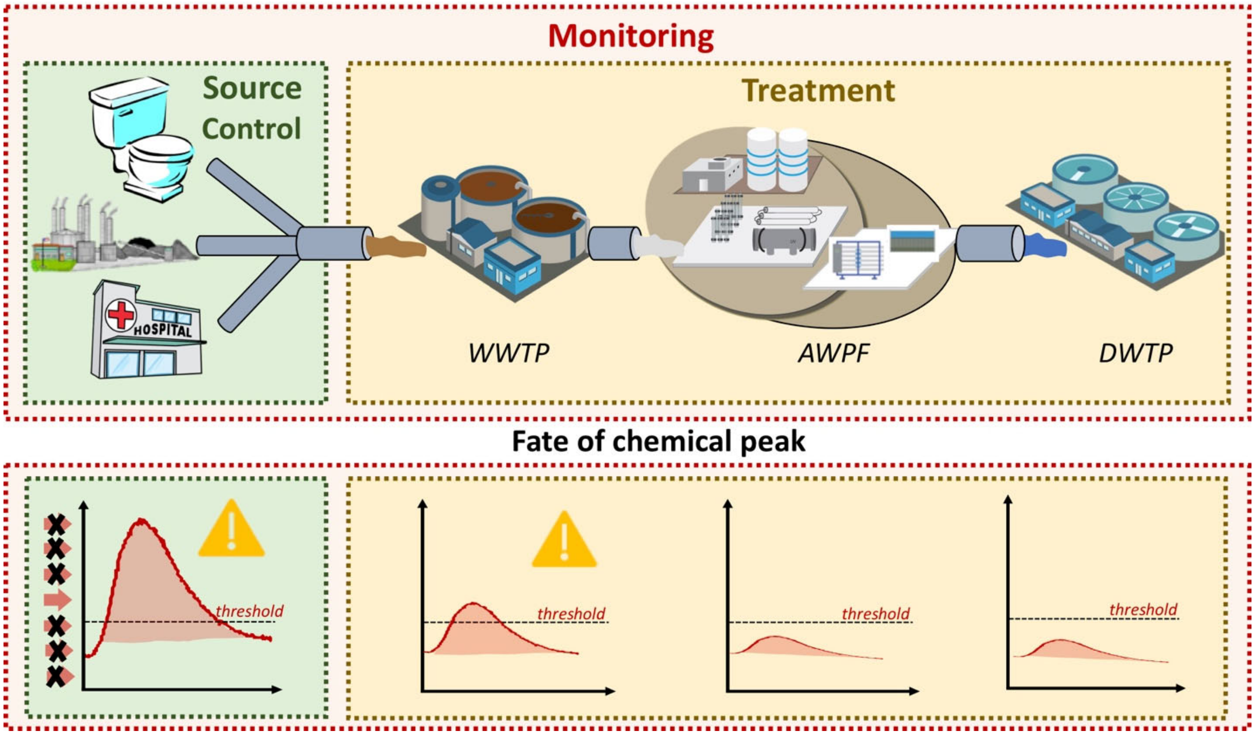

Figure 5-13. Hypothetical Fate of a Chemical Peak for a Raw Water Augmentation without an Environmental or Engineering Buffer DPR Scenario.

5.2.4 Treated Drinking Water Augmentation

Treated drinking water augmentation (TDWA) is a DPR scenario where the advanced treated water produced at the AWPF is directly delivered to the distribution system for consumption, bypassing the DWTP. This is inherently the highest risk DPR scenario regarding public health concern and requires

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[18] There can be RWA scenarios where blending (i.e, comingling of flows in a pipeline) of advanced treated water from potable use with other raw water supplies for drinking water can occur. For example, a project may commit that no more than 10% of the raw water used from the drinking water plant will be from potable reuse. Thus, there could be some scenarios where a degree of blending is provided through this method that is helpful. This will be project specific.

additional studies to demonstrate the feasibility and safety of this practice. If this scenario is to be implemented, it would require a high degree of safeguard components that provide chemical peak "averaging" ability. This would include enhanced source control and monitoring in addition to a robust and reliable AWPF treatment train. Figure 5-14 depicts this DPR scenario, where enhanced source control would proactively diminish the occurrence (and magnitude) of chemical peaks and enhanced monitoring to identify a peak and provide the adequate response time. These features coupled with a well-functioning WWTP and a robust AWPF are used to successfully control and "average" chemical peaks.

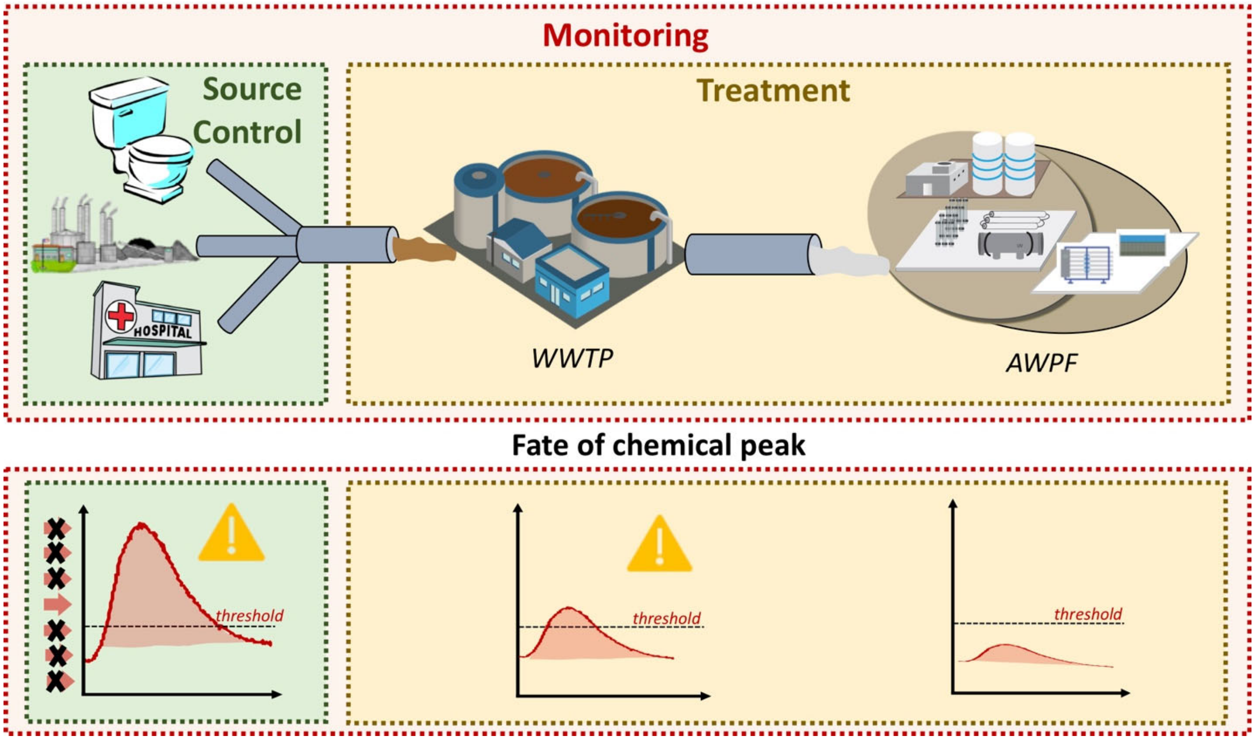

Figure 5-14. Hypothetical Fate of a Chemical Peak for a Treated Drinking Water Augmentation DPR Scenario.

5.2.5 Emphasis on Different Chemical Peak "Averaging" Strategies for DPR Scenarios

Peak averaging is achieved through key strategies that consist of monitoring, source control, treatment, and blending. The previous sections described how peak averaging is achieved for the different DPR scenarios. Qualitatively, Figure 5-15 summarizes the relative emphasis that should be placed on peak averaging strategies for the different DPR scenarios. For example, for DPR scenarios without the option of blending (i.e., RWA without an environmental buffer and TDWA), peak averaging has to be sufficiently achieved through the remaining strategies. Treatment plays a relative bigger role for TDWA when compared to RWA without an environmental buffer. This occurs since TDWA has the two facilities (i.e., WWTP and AWPF) whereas RWA without an environmental buffer has three facilities (WWTP, AWPF, and DWTP) with their own site-specific staff able to identify abnormalities. This indirectly provides more emphasis on monitoring for RWA without an environmental buffer in comparison to TDWA. Detailed programmatic (e.g., source control) and treatment system design is site-specific and outside the scope of the present study and would be included in the engineering design and feasibility review for a DPR facility in collaboration with the regulatory authority.

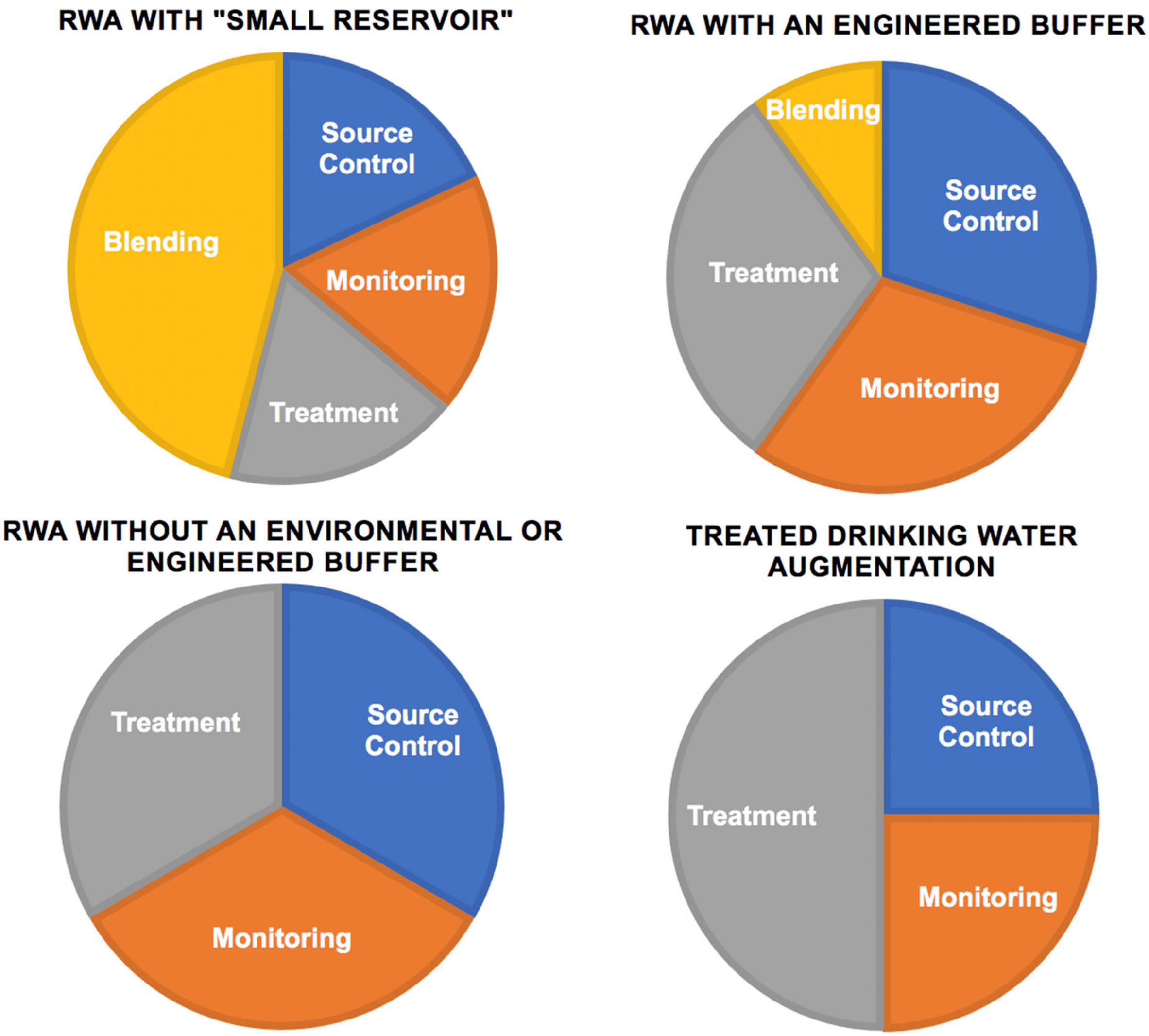

Figure 5-15. Relative Emphasis of Peak "Averaging" Strategies for DPR Scenarios.

CHAPTER 6

Evaluation of TOC Meters

The experimental evaluation of commercially available on-line and bench-top total organic carbon (TOC) meters was performed by the Southern Nevada Water Authority's Applied and Water Quality Research and Development Center. This chapter provides a summary of the results and discusses any potential implications for Direct Potable Reuse projects. The full report is provided in Appendix A.

6.1 Quality Control and Evaluation of TOC Analytical Methods

Prior to the TOC method evaluation described in the next section, a holding and VOC screening study was performed for quality control to determine the extent of any VOC loss during sample storage. A total of 8 unique VOCs were screened, with 5 selected for the TOC performance phase as summarized in Appendix A, Table A-1 and included: 1,2-dichloropropane, acetone, carbon disulfide, dichloromethane (methylene chloride), and methyl isobutyl ketone. VOCs were measured using EPA 524.2 or EPA 8260B methods. The results of the VOC holding study showed the recovery of VOCs in RO Permeate (ROP) and RO Feed (ROF) samples had minimal loss during the preparation of samples and transport to participating utility sites.

A total of 9 participants (A – I) utilizing TOC monitoring in their facilities included 7 unique on-line meters and 4 bench-top meters (see Appendix A, Table A-6). TOC meters included in the study were categorized three ways: high-temperature combustion (HTC), Standard Methods 5310B (Shimadzu TOC-L and TOC 4200), persulfate-ultraviolet oxidation (PUO), Standard Methods 5310C/US EPA 415 (Sievers M9 and M5310C), or a patented Two-Stage Advanced Oxidation (TSAO) accepted by EPA for analysis of water (Hach Biotector B3500 and B7000). Inorganic carbon removal (ICR) was in the form of sparging (HTC and TSAO instrument) or vacuum degassing (PUO instruments). Some meters were tested with ICR on and off generating up to 16 different measurements for ROP and ROF for 5 individual VOC compounds, and VOC mixtures. Each condition was analyzed in triplicate, resulting in 417 total TOC measurements of spiked samples, not including blanks, as well as the System Suitability Testing (SST) performed for both ROF and ROP. The majority of the meters, with the exception of two during testing of ROP, showed response efficiency within the ± 15% efficiency criteria (see Appendix A, Table A-13).

6.2 Review of TOC Meter Performance for Detection of VOCs

VOCs were spiked into representative samples of ROF and ROP and shipped to the participating utilities for their analysis of the samples using their respective TOC instruments. The results of the TOC meter performance for measurement of VOCs are provided in Appendix A, Table A-14. For ROF and ROP, the compound TOC performance recoveries were calculated based on the measured TOC, with the background TOC in the ROP and ROF subtracted out, divided by the initial VOC measured concentrations (as C) as measured by the reference EPA 524.2 and/or EPA 8260B method. Notably, the performance between the HTC, PUO, and TSAO instrument was different for recovery of tested VOCs. There were further differences in performance with and without the ICR step.

For acetone, the on-line PUO instruments with ICR on performed better than the HTC and TSAO analogs, achieving recovery of 74%-81%. There were minimal differences for PUO instrument with ICR on or off for recovery of acetone, while some improvement in recovery was observed for the HTC on-line and bench-top instruments. Notably, the Sievers 5310C, Sievers M9, and Shimadzu 4200 (ICR off during ROF sampling) with on-line TOC meters provided similar recovery of acetone, which has the lowest Henry's Law dimensionless constant, H_{yc}, of 0.00143 according to the EPA CompTox database.

For MIBK, which has a slightly higher H_{yc} of 0.00232 than acetone, the on-line PUO instruments with ICR on performed better than the TSAO analog, achieving recovery of 83%-87% vs. 48% in ROP and 73-76% vs. 17% for ROF. Notably, the HTC instrument, Shimadzu 4200 on-line meter used during ROF testing showed ~ 50% recovery with ICR on and 87% with ICR off. There were minimal differences for PUO instrument with ICR on or off for recovery of MIBK for at least participants A and D using PUO based 5310C TOC instruments. The bench-top HTC instruments demonstrated variable recovery of MIBK between 29% and 75% for ROP and between 29% and 76% for ROF.

For 1,2-dichloropropane, the PUO instruments with ICR on performed significantly better than the TSAO analog, achieving recovery of 77%-84% vs. 5% in ROP. The relatively poor recovery observed on the TSAO instrument appeared to be due to the ICR step. Considering that 1,2-dichloropropane is more volatile than acetone and MIBK with H_{yc} of 0.115, turning ICR off provided a higher recovery for the bench-top HTC instrument (39% recovery) and for the PUO instrument 5310C (recovery increased to 98%). This indicates that with increased volatility, ICR step introduced some losses of 1,2-dichloropropane, while still providing sufficient analytical response to ascertain TOC meter's performance.

For dichloromethane, which has an H_{yc} value of 0.133, the observed recoveries were lower than those observed for 1,2-dichloropropane, however similarly, PUO instruments (with ICR on) again performed better than the TSAO analog, achieving recoveries of 55%-82% vs. 3% in ROP. Turning the ICR off provided a greater difference in performance, than that for 1,2-dichloropropane. The PUO based instrument, M5310C, demonstrated a recovery of up to 87% with ICR off in ROP. In ROF, PUO based instruments demonstrated a recovery of 52%-60%, while both HTC and TSAO analogs had a recovery of 0%. With ICR off, PUO based M5310C instrument again showed an improved recovery of 74% (vs. 54% with ICR off) for ROF.

For Carbon disulfide, poor recoveries were observed for all the online analyzers for both ROP and ROF with an overall average of 7%. This indicates that ICR step provides significant removal of carbon disulfide, which has the highest H_{yc} of 0.589. With ICR off, recoveries improved to 17%-57% among the tested instruments.

For the VOC mixture that contained all five of the above-described VOCs, the PUO instruments with ICR on generally performed better than the HTC and HTC better than the TSAO analog (up to 70% for PUO vs. 37% for HTC and 25% for TSAO instruments), as was also noted by demonstrated recoveries of individual compounds in both ROF and ROP. There was some improvement for PUO instruments with ICR off for recovery of VOC mixture, with up to 83% recovery and up to 85% for an HTC instrument. Some improvement in recovery was also observed for the HTC bench-top instruments (up to 77%-79% with ICR off vs. 27%-62% with ICR on).

For the five tested VOCs, the hydroxyl rate constant varied between $10^7 – 10^9$ M^{-1} s^{-1} and was found to have no correlation with the VOC recovery. In addition, the SST showed the response efficiency for oxidation of sucrose vs. 1,4-benzoquinone was within the ± 15% efficiency criteria for all but two instruments for ROF. The H_{yc} however was observed to impact the VOC recovery, where above H_{yc} ~ 0.2, recovery dropped off significantly and for carbon disulfide (H_{yc} 0.589) recovery was down to 2-5% for ROP.

6.3 VOC Removals by Secondary Treatment and Dependence of Henry’s Law Constant (H_{yc})

Henry’s Law Solubility constant, Hcp (SI units mol m^{-3} Pa^{-1}), and Volatility constants, KHpc (SI unit Pa m^3 mol^{-1}), were obtained from US EPA CompTox Chemical Dashboard and cross-referenced with available literature, mainly Sander 2015 (US EPA 2020a, Sander 2015). The unitless Henry’s Law Constant, H_{yc}, as a ratio of concentration in the gas to the aqueous phase concentration, is sometimes referred to as the “air-water partitioning coefficient” and reflects the relative volatility of a substance (i.e., volatilizing from water into air) with greater H_{yc} denoting greater volatility. H_{yc} was determined by using either the available Hcp or KHpc data and calculated using the following formulas:

$$K_H^{pc} = \frac{1}{H^{cp}}$$

$$H_{yc} = \frac{1}{H^{cp}RT}$$

Where, R = 8.314 $m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$ (or $8.206 \cdot 10^{-5}$ $m^3 \cdot atm \cdot K^{-1} \cdot mol^{-1}$)
T = 298.15 K (25 °C)
Hcp in units of mol m^{-3} Pa^{-1}

H_{yc} is commonly used as a design parameter for air-stripping processes to optimize removal. During wastewater treatment, the secondary process’ primary function is to transfer oxygen from gas into dissolved form, so that it is available for bacteria to breakdown organics (biochemical oxygen demand) and promote nitrification. The oxygen transfer is typically less than 10%, and thus significant amounts of air are needed to transfer the required amount of oxygen into liquid phase. For reference, a typical air to water ratio for achieving nitrification is on the order of 10:1. As a result, secondary aeration can provide removal of certain VOCs.

During the case study evaluations in Chapter 4, VOCs concentrations were evaluated to assess apparent removal through the secondary wastewater treatment process. VOC removal data from the Orange County Sanitation District and the City of San Diego’s North City Water Reclamation Plant were calculated based on the difference in the VOC concentrations in the influent and secondary effluent (see Table 4-7 and Table 4-9). The data was further sorted to only include the percent removals based on detected VOC concentrations in the effluent and plotted as a function of H_{yc}. These data are shown in Figure 6-1 and include the observed removals of methylene chloride, toluene, m,p-xylenes, and acetone. This observed removal was modeled using a conservative secondary treatment air to water ratio of 3.25 and calculating removal as a function of H_{yc} values.

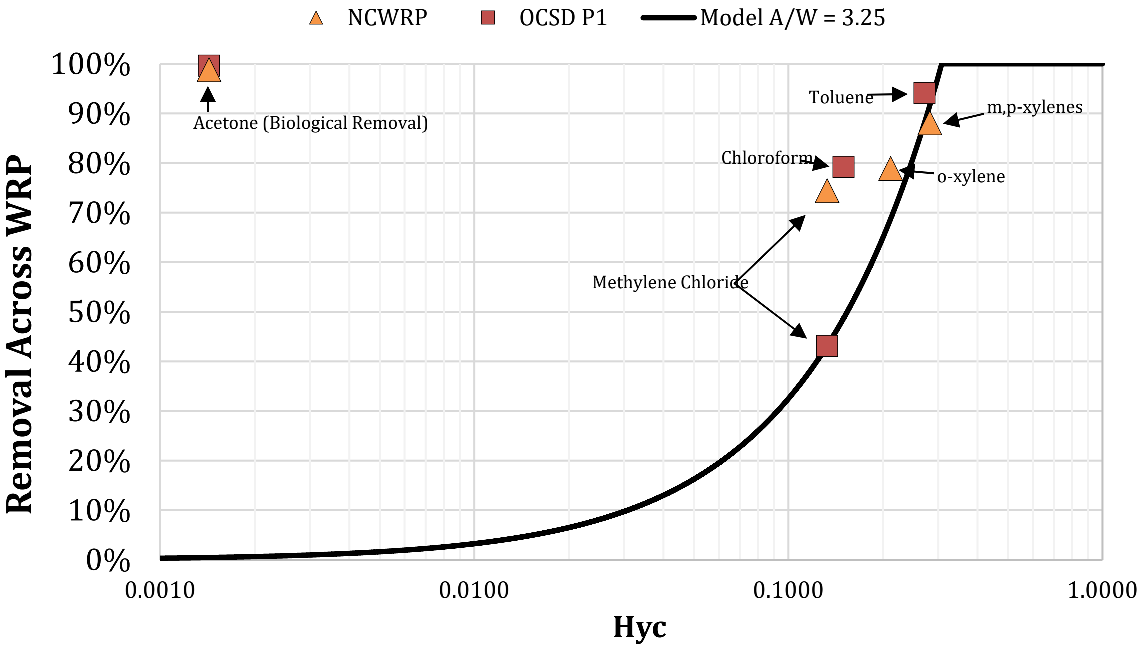

Figure 6-1. Relative VOC Removal as a Function of H_{yc} from Two Full-Scale Facilities in CA.

Based on this data there is an expected increase in VOC removal for compounds with higher H_{yc}. While there is some variability between the two facilities, generally VOC removals in both cases increased for compounds with higher H_{yc}. Acetone removal was observed at greater than 98.8% and 99.6%, which is likely attributed to biological degradation as the H_{yc} value is relatively low for acetone. On the other hand, toluene with H_{yc} of 0.269 was removed by 94.1% and for compounds with H_{yc} higher than 0.305 a removal greater than 99.0% removal can be expected, while for compounds with H_{yc} of > 0.308 a 99.9% removal can be expected based on the model. For facilities treating for BOD removal and achieving complete nitrification with higher apparent air to water ratios, there is a potential for greater removal of VOCs with lower H_{yc} as indicated by the data shown in Figure 6-2 which indicates modeled removal based on the apparent Air/Water ratio (A/W). This information supports the likelihood of VOCs removal by the wastewater treatment that precedes advanced purification for potable reuse, discussed further below.

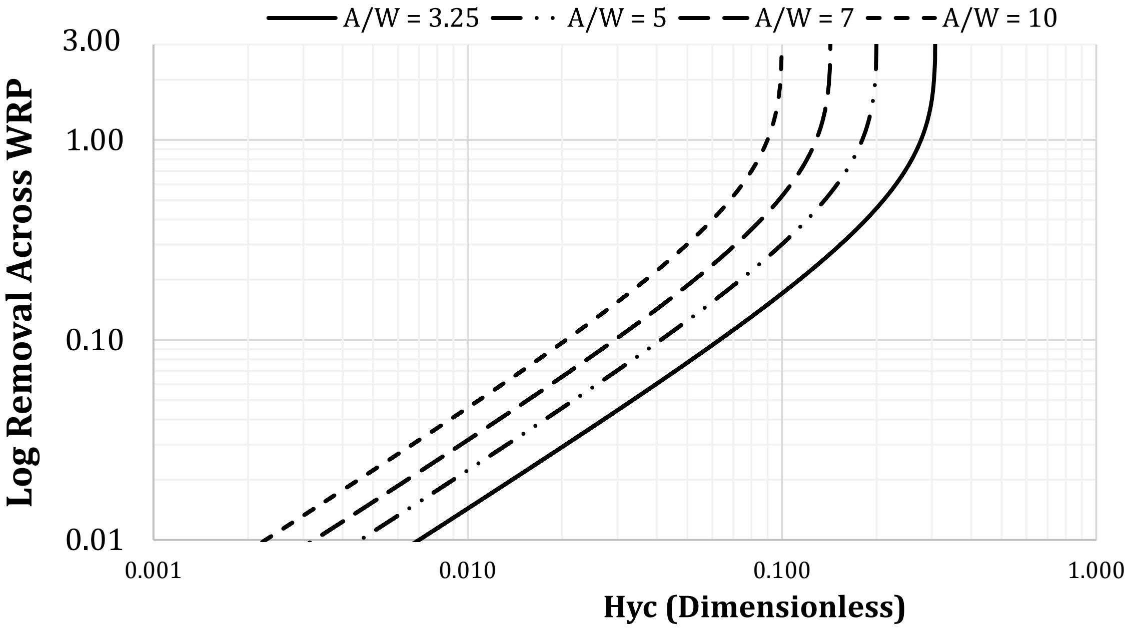

Figure 6-2. Expected VOC Removal at Different Air to Water Ratios (A/W) and as a Function of H_{yc}.

6.4 Implications of Findings for Detection of Chemical Peaks

The Standard Method 5310 and EPA 415.3 discuss the definitions of and requirements for TOC measurements (SM 2015, US EPA 2009). Fundamentally, total organic carbon includes particulate organic carbon, dissolved organic carbon and purgeable organic carbon. Purgeable organic carbon is typically present at negligible concentrations in natural waters and current TOC methods such as those based on SM 5310 and EPA 415.3 define TOC as the non-purgeable organic carbon (NPOC). Further, EPA 415.3 method states that inorganic carbon must be removed (purged) prior to total organic carbon measurement, or “if the IC is not completely removed, significant error will occur” (US EPA 2009). As identified in Appendix A, TOC meters employing persulfate-ultraviolet oxidation, specifically Sievers 5310C or Sievers M9, commonly include an inorganic carbon removal (ICR) accessory to decrease the levels of inorganic carbon in the sample stream, prior to analysis for inorganic and total carbon. The ICR accessory is not required for the determination of TOC, especially when the TOC concentration is comparable to the inorganic carbon concentration in the sample. The ICR accessory is recommended when the TOC concentration in the sample is less than 10% of inorganic carbon concentration. Since TOC is measured by difference of TC and IC, lowering IC by 95% before analysis, improves the accuracy and precision of measuring TOC, and allowing lower detection limits. Although the experimentation suggested that the recovery of higher H_{yc} compounds (i.e., more volatile compounds) was better without ICR, attempting to use such meters without the required accessory will be outside the manufacturer and method intended purpose and may compromise TOC meter ability to provide accurate readings of TOC removal by reverse osmosis membranes.

During the case study literature review, it was identified that TOC meters, such as the Sievers 5310C and M9, detected chemical peaks for various compounds, such as: acetone, methyl isobutyl ketone (MIBK), N,N-dimethylacetamide (DMAc), and a mixture of 1,4-dioxane, formaldehyde, and *N*-nitrosodimethylamine (NDMA). Similarly, the experimental evaluation of TOC meters (Appendix A) showed recoveries of volatile compounds such as acetone (H_{yc} 0.00143), MIBK (H_{yc} 0.00232), and 1,2-dichloropropane (H_{yc} 0.115) were within ± 20% of spiked concentrations as verified by reference methods (EPA 524.2 and/or EPA 8260B) for certain meters. For methylene chloride (H_{yc} of 0.133) at least some TOC meters demonstrated recovery of 55-59%. At a recovery rate of 50%, the measured concentration would be one half of the true value. While this may not be ideal from a quantitative analysis standpoint, the ability to detect a chemical peak during monitoring of advanced treatment is not significantly compromised. This highlights the versatility of TOC meters to detect various volatile and purgeable organic compounds matching and even exceeding the expectations of SM5310 and EPA 415.3 method's definition of TOC as NPOC.

However, for the more purgeable compound carbon disulfide (H_{yc} 0.589), the recovery was only 2-5%. Significant reduction in TOC recoveries was observed for compounds above H_{yc} of 0.2. While the exact threshold for transition from NPOC to POC in terms of H_{yc} is not defined, there does appear at least some overlap for current TOC meters to provide some level of detection for purgeable compounds. This is due to the fact that volatile organics, defined as organic compounds with a boiling point of 250° C or below, have different degrees of purgeability, that may be defined by H_{yc}. While it may be generally considered that compounds are more volatile based on the boiling point of vapor pressure as shown in Figure 6-3, H_{yc} does not directly depend on the boiling point. Similarly, while generally lower molecular weight volatile organic compounds have a lower log Kow, which would indicate compounds are more hydrophilic and more miscible with water, there is no correlation of molecular weight with H_{yc}. Therefore, volatile organic compounds should be evaluated for H_{yc} value independently, when assessing purgeability.

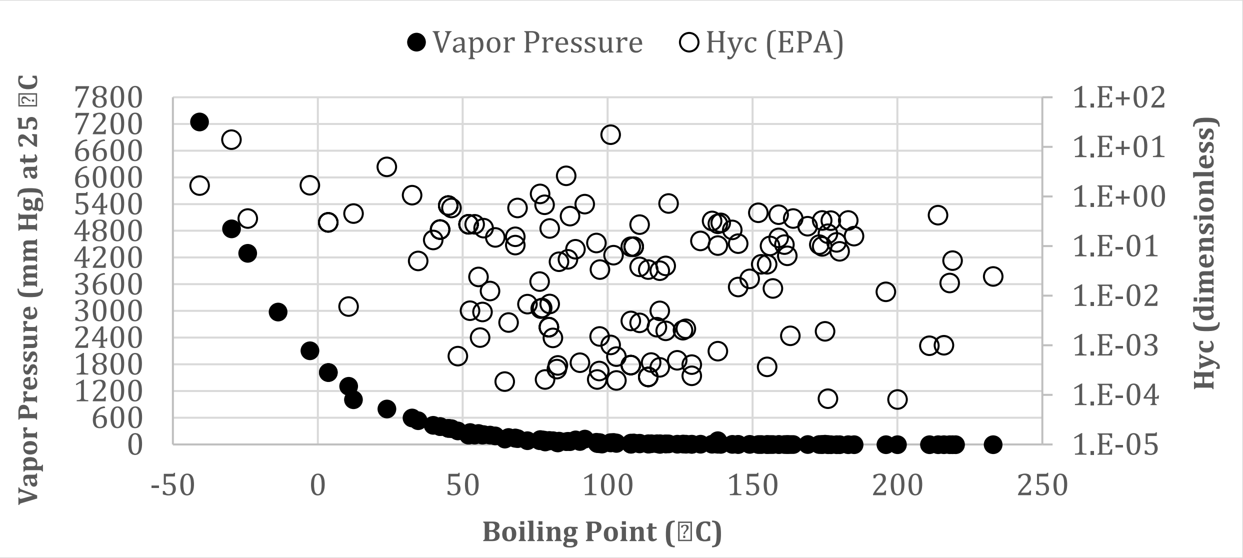

Figure 6-3. Vapor Pressure and H_{yc} for Different VOCs Varying by Boiling Point.

The apparent removal of VOCs by the upstream wastewater treatment facility would suggest that the secondary treatment process, which includes both biological degradation and air stripping capacity, provides an additional barrier of these types of organics. The removal is especially effective for compounds with higher H_{yc} above 0.2. In addition, compounds with molecular weight above 200 g/mol are expected to be well removed by reverse osmosis filtration, which further reduces the types of expected VOCs that may be present in RO permeate. Provided that the tested TOC meters showed at least 50% recovery for detection of compounds with H_{yc} up to 0.133, there is reasonable expectation of the ability of current commercial TOC meters to detect chemical peaks originating from volatile organic compounds.

6.5 Recommendations on the Use of TOC Meters for DPR Projects

Current available and accepted methods for measurement of TOC in water, source water, and wastewater rely on accurate determination and/or removal of inorganic carbon. It is understood that during the instrument's determination or removal of the inorganic carbon, the process has potential to lose some purgeable organics. Therefore, TOC methods commonly measure NPOC as TOC.

Almost all of the commercial TOC meters that were tested during this project showed excellent ability to measure NPOC as demonstrated by the system suitability testing and demonstrated acceptable performance of measurement of VOCs with H_{yc} of less than or equal to 0.133 with at least 50% recovery (and often greater). Purgeable organics are diverse in chemical properties including boiling point and vapor pressure, water solubility, miscibility with water, and purgeability. Detection of highly purgeable compounds ($H_{yc} > 0.2$) by TOC meters may be limited, however, the probability of such compounds to remain after upstream wastewater treatment at appreciable concentrations is low and of lesser concern due to their removal during aeration, limited water solubility and miscibility. Source control programs from the case studies were effective at reducing the number and extent of chemical peaks observed by reclamation and advanced water purification facilities (Section 4.3). The observed performance of TOC meters evaluated in this study is adequate for expected VOCs that may remain post-upstream wastewater aeration and biological processes and reverse osmosis filtration. Greater detail of individual instrument performance can be found in Appendix A.

CHAPTER 7

Summary and Recommendations

This project is the fourth of five research projects supporting the California SWRCB to develop criteria and guidelines for DPR. Illicit short-term discharges of chemicals into the wastewater sewershed have the potential to compromise final product water quality distributed by a potable reuse facility. As such, it is necessary to consider a complimentary range of strategies that can be used to “average” (dampen) such potential chemical peaks for different DPR scenarios.

This project evaluated the potential for certain chemicals to persist through advanced water treatment systems and options for the detection of such chemical peaks. It also developed criteria for differentiating chemical peaks from normal facility variations, and evaluated treatment and blending options. The project reviewed source control programs from case study utilities, evaluated TOC analyzers for VOC detection and quantification, discussed documented chemical peaks, and discussed implications of chemical peaks to different DPR scenarios.

A short list of chemical families were identified as having intermediate to poor rejection by RO membranes *as well as* poor removal by AOP (less efficient than 1,4-dioxane): low molecular weight (LMW) haloalkanes, LMW alcohols, aldehydes, and ketones, acetonitrile, methylisothiocyanate (MITC), and trihalomethanes (THMs). Industrial use of solvents including LMW haloalkanes, alcohols, aldehydes, ketones, and acetonitrile make these the compounds with the highest potential to occur as a chemical peak persisting through FAT.

Ultimately, the report identifies four key strategies that can be used to “average” chemical peaks:

1. Source control
2. Monitoring
3. Treatment
4. Blending

Because these strategies “average” chemical peaks in different ways, it is important to evaluate all options and incorporate a balanced approach that fosters a reliable DPR implementation to control chemical peaks. Treatment alone may be insufficient to control (“average”) chemical peaks, and it is important to also incorporate an enhanced source control program that proactively deters and diminishes the occurrence of peak dischargers. Similarly, blending from a “small reservoir” may be sufficient to average a high-volume illicit discharge, but without monitoring it is not possible to verify the extent of blending and assure if averaging to levels below concern were achieved. In essence, each peak averaging strategy should be viewed distinctly, and applied in a balanced manner when possible.

Blending can be very effective at peak averaging when available and it is non-selective to the chemical type in doing so. However, blending is not available for DPR scenarios that do not utilize an environmental or engineered buffer (i.e., RWA with no buffer and TDWA). For such DPR scenarios, it is inherent that the remaining averaging strategies need to be enhanced. The AWPF would need to provide sufficient robustness and treatment redundancy to account for the lack of blending. Additional treatment barriers in conjunction with FAT should be considered to increase robustness in reducing the concentration of chemical constituents. Examples of such barriers along with their additional benefits include:

1. Ozone/BAC Pretreatment
    a. Can also provide disinfection, provide low molecular weight biomass ready to be consumed by downstream BAC, and removal of CECs
2. Air Stripping
    a. Along with peak averaging, can also provide stripping of volatile DBPs
3. Activated Carbon
    a. Can also provide increased TOC reduction and removal of CECs
4. Additional RO/AOP treatment
    a. Also provides additional pathogen reduction, CEC removal

Enhanced monitoring along with source control is also critical for DPR scenarios lacking an environmental or engineered buffer. These two components "average" peaks in an indirect manner, helping mitigate both the occurrence and magnitude of chemical peaks. A tailored source control monitoring program serves as a preventative measure for controlling peak events, and along with enhanced monitoring can help identify the source of an illicit discharge. These two components (enhanced monitoring and source control), when effectively implemented, can offer deterrence of chemical peaks. That said, DPR facilities should have failure response protocols (including diversions) that can be applied should catastrophic events occur.

For the DPR scenarios that can "average" chemical peaks through blending, analysis of the worst chemical peak observed from the case study utilities showed blending can be very effective at peak averaging. A buffer with less than 24 hours theoretical retention time offered limited peak averaging but still provided some peak dampening (e.g., 60% reduction in the theoretical scenario that was developed), with significantly more limited peak averaging as the theoretical retention time is decreased. On the other hand, "small reservoirs," identified as reservoirs with less than 60 days of hydraulic residence time, offer significant peak averaging. From the analysis in this study's theoretical scenario, a "small reservoir" with a theoretical retention time of 10 days was sufficient to "average" peak concentrations to levels below those permissible per current IPR regulations. As such, DPR applications that have the option to use "small reservoirs" should consider its blending effects for chemical peak averaging when possible.

In summary, the project recommendations are:

1. A definition of a chemical peak (Chapter 3) is recommended to differentiate normal facility variation in water quality from true chemical peaks. In this study, chemical peaks are defined as resulting from intentional or unintentional illicit discharges of chemicals to the sewershed.
2. Online monitoring of TOC (Chapters 4 and 6) is recommended as a feasible option for capturing chemical peaks. TOC is already used as a critical control point (CCP) monitoring device for RO systems related to compliance.
3. Experimental results suggest that commercially available TOC analyzers have the ability to detect chemical peaks originating from volatile organic compounds (Chapter 6 and Appendix A). Amongst the TOC meters that were tested, at least two models demonstrated acceptable performance and are recommended for DPR projects.
4. Given that chemical peaks are expected to last on the order of hours to days, no more frequent than a fifteen minute minimum sampling interval is recommended for the online TOC analyzers (Chapter 3).
5. Due to the very limited expected frequency of chemical peaks (< 0.5% of case study data evaluated), periodic grab sampling (e.g., weekly, monthly, quarterly) for compounds known to potentially

escape FAT is not recommended for DPR for the explicit purpose of discovering an illicit discharge (Chapters 3 and 4).

6. Utilities should prepare a formal TOC response protocol in the event of a TOC peak (Chapter 4). A tiered response protocol may be used to define actions taken depending on characteristics of the event (i.e., TOC concentration and duration). As part of a response protocol, grab sampling is recommended when a peak has been observed and confirmed by the TOC analyzers in an effort to identify the responsible chemical(s) and inform the source control program.
7. An enhanced source control program is recommended for DPR that proactively deters and diminishes the occurrence of chemical discharges (Chapter 4). A tailored source control monitoring program that is continually improved serves as a preventative measure for controlling peak events, and along with enhanced monitoring (e.g., sewershed, on-line, etc.) can help identify the source of an illicit discharge.
8. Additional treatment barriers in conjunction with FAT should be considered to increase robustness and further reduce the concentration of chemical constituents (Chapter 3). Examples of such barriers include ozone/BAC, air stripping, activated carbon, and additional RO and/or AOP.
9. DPR applications that have the option to use “small reservoirs” should consider doing so given the benefits of small reservoirs for chemical peak “averaging” (Chapter 5) due to blending.
10. Utilities considering DPR should pursue a balanced approach to control chemical peaks that includes an appropriate combination of two or more of the following: source control, enhanced monitoring, additional treatment barriers, and/or blending (Chapter 5).

APPENDIX A

Defining Potential Chemical Peaks and Management Options: Experimentation to Address Knowledge Gaps

This appendix was prepared by The Southern Nevada Water Authority.

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A.1 Introduction

The California State Water Resources Control Board has been working to fill knowledge gaps for developing criteria for direct potable reuse (DPR). Reverse osmosis (RO) is a commonly used treatment barrier during potable water reuse treatment applications. Because of their non-porous nature, reverse osmosis membranes can remove a wide range of contaminants including pathogens, organic chemicals, pharmaceutically active compounds, and endocrine disrupting compounds (Yang et al. 2016; Snyder et al. 2007b). However, low molecular weight compounds with uncharged chemical structures still have potential to pass through reverse osmosis membranes during potable water reuse applications (Breitner et al. 2019; Linge et al. 2012; Marron et al. 2020). For example, at Orange County Water District's Groundwater Replenishment System in California, researchers detected a spike of total organic carbon (TOC) in the RO permeate which was later attributed to acetone (Marron et al. 2019). To capture unwanted chemical spikes in the RO permeate during DPR applications, it is recommended that surrogate parameters, such as TOC, should be monitored online (Bernados 2018).

Current online TOC detection instruments are UV-absorption-based or oxidation-based. However, UV absorption-based systems only capture UV-absorbing compounds, such as UV-absorbing aromatic compounds in natural organic matter. Non-UV-absorbing compounds would not be detected. Currently employed online oxidation-based instruments use three main steps: 1) either complete removal of inorganic carbon (IC) before analysis as sample pretreatment (i.e., Hach and Shimadzu instruments), or partial removal of IC (>95%) followed by IC measurement (i.e., Sievers); 2) oxidation of organic compounds in the sample to carbon dioxide (CO_2); 3) quantification of the oxidized carbon (CO_2) as Total Carbon (TC) = TOC (i.e., Hach and Shimadzu instruments) or subtraction of IC from TC to determine TOC (i.e., TOC = TC – IC) (i.e., Sievers) and presenting the results in units of carbon per volume of sample (mg/L).

Complete or partial removal of IC is critical to accurately measure TOC. If the IC is not completely removed during analysis, significant error may occur in the TOC result, particularly for waters with high IC and relatively low TOC. For example, the Hach and Shimadzu instruments require complete removal of IC in order to directly measure TOC. However, since the Sievers instrument measures the TOC by subtraction of IC from TC, partial removal of IC is commonly used to increase the accuracy of the TOC calculation. Therefore, for IC removal (and direct measurement of IC for Sievers instruments) the sample is initially acidified. Then the CO_2 is either degassed with a Teflon degassing module (i.e., Sievers Inorganic Carbon Remover (ICR) module) or it is purged, typically either with oxygen, ultrapure air, or nitrogen (inorganic carbon sparging (ICS)) (Hach and Shimadzu). During the degassing of IC, there is the potential for unintentional stripping of volatile organic compounds (VOCs). For this reason, some instruments report the TOC results as non-purgeable organic carbon (NPOC).

Oxidation of organic carbon is typically performed with one of the current methods:

1. Catalytic combustion – sample is injected into an oxidation column filled with catalyst and heated to high temperatures (~700-800°C) to convert organic compounds to CO_2 (SM 5310B) (i.e., Shimadzu)
2. Photocatalytic oxidation – organic compounds are converted to CO_2 in the presence of UV light and an oxidant, such as ammonium persulfate (SM 5310C, EPA 415) (i.e., Sievers)
3. Chemical oxidation – sample is mixed with an oxidant and subjected to conditions that promote conversion of organic compounds to CO_2 (e.g., high pH and Ozone) (i.e., Hach)

The photocatalytic oxidation and catalytic combustion methods are currently the most common methods for laboratory and on-line TOC analysis techniques for the analysis of water and wastewater. Catalytic combustion (SM 5310B) analysis has a long track record in both water and wastewater applications where the TOC range is typically above 4 µg/L and up to 30,000 mg/L (i.e., Shimadzu TOC-L). Photocatalytic oxidation methods (SM 5310C and EPA 415) provide comparable detection limits (i.e., Sievers M5310C) or lower (i.e., Sievers M9), which are used for applications in clean and ultra-pure water serving a wide range of industries including pharmaceutical, semiconductor, and water purification. Both oxidation methods are used in commercially available online TOC analyzers that may be used at potable reuse facilities.

Oxidized organic compounds are converted to CO_2 or bicarbonate ion and CO_2 is detected by a non-dispersive infrared (NDIR) detector (i.e., Hach and Shimadzu), or is detected by a conductivity detector with a selective membrane for CO_2 which then becomes carbonic acid, dissociating into the hydrogen (H^+) and bicarbonate ions (HCO_3^-) (i.e., Sievers).

Current online analyzers rely on removing IC to accurately measure TOC, which may also remove volatile organic compounds (VOCs). Therefore, the objective of this study was to determine if current online and laboratory oxidation-based TOC analyzers can detect specific organic chemicals and measure them as TOC, particularly those that may pass through reverse osmosis (i.e., low molecular weight), and are volatile or resistant to oxidation. The study performed the following two main tasks:

1. Select target VOCs and perform preliminary holding studies to determine conditions to minimize compound loss from samples spiked with VOCs that would be transported from the SNWA laboratory to participants for the following Task.
2. Conduct a performance evaluation for commercially available online and bench-top TOC analyzers for their effectiveness to measure VOCs in RO permeate (ROP) and RO feed (ROF). ROF was evaluated since this could be another location to employ a TOC analyzer at RO facilities. TOC analysis was conducted onsite by participants.

A.2 Methods and Approach

A.2.1 Selection of Target VOCs

Five target compounds [dichloromethane (DCM), methyl isobutyl ketone (MIBK), acetone, 1,2-dichloropropane, and carbon disulfide] were selected for the holding study and TOC analyzer performance evaluations (Table A-1). These compounds were selected based on four criteria: (1) a range of reactivity with hydroxyl radicals (Table A-2), the primary oxidants in the Sievers and Hach oxidation methods; (2) moderate to high volatility [i.e., Henry's law constant (H_{yc}) <1.1]; (3) aqueous solubility greater than 0.5 mg/L as C; and (4) known or suspected partial RO pass-through due to molecular weight less than 113 g/mol and neutral charge (Breitner et al. 2018; Rodriguez et al. 2012; Kibler et al. 2020; Marron et al. 2019). Furthermore, all five of these compounds have industrial applications as solvents or chemical synthesis precursors so intermittent, high-concentration emissions to municipal sewersheds are plausible (National Library of Medicine 2020). DCM and 1,2-dichloropropane have USEPA primary maximum contaminant levels and carbon disulfide and MIBK have California notification levels (USEPA 2020b; California Water Boards 2020). Acetone has relatively low toxicity with an oral chronic reference doses of 0.9 mg/kg/day but could cause taste and odor issues (Galloway et al. 2020; National Library of Medicine 2020; Marron et al. 2019). Vinyl chloride was considered but omitted since it was only available for purchase in methanol solution, which would contribute additional carbon to the samples. Carbon tetrachloride and toluene were considered but omitted due to insufficient solubility. Vinyl chloride (≧99.5%), toluene (≧99.5%), 1,2-dichloropropane (99%), carbon tetrachloride (≧99.9%), carbon disulfide (≧99.9%), methylene chloride (dichloromethane [DCM]) (≧99.8%), methyl isobutyl ketone (MIBK) (≧99.5%), and acetone (≧99.9%) were purchased from Sigma Aldrich.

Table A-1. List of Compounds and Their Chemical Properties Used in This Study.

Target Compound	Molecular Formula	M.W (g/mol)	Density (g/cm^3)	Solubility in Water (mg/L)	H_{yc}	Screening Phase[d]	VOC Holding Phase[e]	TOC Performance Phase[f]
Vinyl Chloride	C_2H_3Cl	62.5	0.91	2700	1.048	Tested		
Toluene	C_7H_8	92.1	0.87	526	0.269	Tested		
Carbon Tetrachloride	CCl_4	153.8	1.59	559[b]	1.080	Tested		
Dichloromethane	CH_2Cl_2	84.9	1.33	13000	0.124	Tested	Tested	Tested
Methyl isobutyl ketone	$C_6H_{12}O$	100.2	0.80	19100	0.010	Tested	Tested	Tested
Acetone	C_3H_6O	58.1	0.79	1005130[a] (Miscible)	0.014	Tested	Tested	Tested
1,2-Dichloropropane	$C_3H_6Cl_2$	113.0	1.16	2800	0.120			Tested
Carbon Disulfide	CS_2	76.2	1.26	2160	0.661			Tested
Sucrose	$C_{12}H_{22}O_{11}$	342.3	1.59	2100000[c] (Miscible)	NA			
1,4-Benzoquinone	$C_6H_4O_2$	108.1	1.32	11000	0.019			

[a] National Center for Computational Toxicology (NCCT) Office of Research and Development, US EPA. https://comptox.epa.gov/dashboard/DTXSID8021482

Tested

[b] Chen et al. 2012

[c] Yalkowsky and Dannenfelser 1992

Tested

[d] Screening: 6 different compounds were tested for their solubilities.

Tested

[e] Holding: The recoveries of selected compounds were tested under varying holding times and temperatures.

[f] Round robin study between participants.

Table A-2. Classification Bins for Selected Compounds Based on Henry's Law and Hydroxyl Radical Rate Constants.

k_{*OH}, L/Mol-s	$H_{yc} > 0.5$	$0.1 < H_{yc} < 0.5$	$0.01 < H_{yc} < 0.1$
$k_{*OH} > 1 \times 10^9$	Carbon Disulfide		MIBK
$1 \times 10^8 < k_{*OH} < 1 \times 10^9$		1,2-Dichloropropane	Acetone
$1 \times 10^7 < k_{*OH} < 1 \times 10^8$		Dichloromethane	

A.2.2 Water Matrix

RO permeate and feed waters were collected and shipped by Orange County Water District (OCWD). Samples were collected from their full-scale RO operation. RO permeate was collected on 01/08/2020 for the preliminary VOC holding and the inter-laboratory comparison studies and 05/20/2020 for the TOC analyzer performance evaluation. RO feed was collected on 06/30/2020 for the TOC analyzer performance evaluation. The samples were collected in glass containers for the holding study and polypropylene containers for the TOC instrument performance evaluations and shipped overnight to SNWA. Samples were stored at 4°C until used.

A.2.3 TOC Analytical Methods and Analyzers

TOC was measured by online and bench-top instruments listed in Table A-3. The instruments employ high-temperature combustion (HTC), Standard Methods 5310B (Shimadzu TOC-L and TOC 4200), persulfate-ultraviolet oxidation (PUO), Standard Methods 5310C/US EPA 415 (Sievers M9 and M5310C), or patented Two-Stage Advanced Oxidation (TSAO) (Hach Biotector B3500 and B7000). The TOC methods that use HTC and TSAO require all of the IC to be removed from the sample before the sample is analyzed for organic carbon content. The IC interference is removed by converting IC to CO_2 by acidification and sparging with high-purity air or oxygen (e.g., Hach instruments use air that passes through an oxygen concentrator to make 90-95% oxygen for sparging). For HTC and TSAO methods, once the sample is free from IC interference, it is then injected into an oxidation chamber of the instrument system. The organic carbon is oxidized to CO_2 by HTC or TSAO that uses ozone and a base reagent to promote the production of hydroxyl radicals. For TOC methods with PUO, a sample injection loop is used with no oxidation step to measure IC directly in parallel with the oxidation step that measures TC. For both PUO steps the IC interference is converted beforehand to CO_2 by acidification and removed partially with a gas permeable membrane. For the PUO oxidation step the acidified sample is added with oxidant (persulfate) into the reaction chamber, where it is exposed to UV light (promoting the production of hydroxyl radicals), converting organic carbon to CO_2. Then the CO_2 is detected by a non-dispersive infra-red (NDIR) detector for HTC and TSAO methods (Shimadzu and Biotector instruments) or a membrane-conductometric detector (Sievers instruments).

Table A-3. On-Line and Benchtop TOC Meters Evaluated in This Study.

Make	Model	Online or Benchtop	Sample Size (mL)	Degas Method	Oxidant	Acid	DL (µg/L)
Suez / Sievers	M5310C	Online & Benchtop	40	Membrane Module	PUO: UV with 15% $(NH_4)_2S_2O_8$	H_3PO_4 (6M)	4
Suez / Sievers	M9	Online	40	Membrane Module	PUO: UV with 15% $(NH_4)_2S_2O_8$	H_3PO_4 (6M)	0.03
Hach	B7000	Online	500	Purge with O_2	TSAO: O_3/NaOH	H_2SO_4 (Conc.)	600
Hach	B3500	Online	500	Purge with O_2	TSAO: O_3/NaOH	H_2SO_4 (Conc.)	60
Shimadzu	TOC-L	Benchtop	40	Purge with Air	HTC: Heat/ Pt Catalyst	HCL (10%)	4
Shimadzu	TOC-4200	Online	20	Purge with Air	HTC: Heat/ Pt Catalyst	HCL (10%)	0.1

A.2.4 VOC Analytical Methods

VOCs were measured by SNWA using EPA Method 524.2, by Eurofins Eaton Analytical, LLC using EPA Method 524.2 and by Silver State (SS) Analytical Laboratories, Inc. using EPA Method 8260B. Eurofins Eaton Analytical and Silver State Analytical Laboratories are certified laboratories.

A.2.5 QA/QC

All standard preparation and sampling were performed using nitrile gloves to prevent contamination. Samples were collected in specially cleaned and silanized glass amber vials with Teflon-lined caps to ensure sample integrity. A concerted effort was made to ensure there was no headspace in any sample container. TOC samples in this study were preserved with hydrochloric acid (HCl), sulfuric acid (H_2SO_4), or phosphoric acid (H_3PO_3), respectively, to pH <2 and stored at 4°C until analysis. VOC samples were acidified to pH 2 with hydrochloric acid (HCl). Sample events and all shipments included quality control samples, at least one reagent blank (trip or equipment blank) and replicates.

A.2.6 Preliminary VOC Holding Study

Preliminary holding studies were conducted to determine conditions to minimize compound loss from samples spiked with VOCs that would be transported from the SNWA laboratory to other participating laboratories. Conditions of concern were the procedure for transferring solution from the spiked stock solution to individual sample vials and potential impact of variable temperature during transport.

Holding times of 1 and 7 days at 4 and 25°C were evaluated. Initially, solutions with target compounds were prepared using OCWD RO permeate and five targeted VOCs: 1,2-dichloropropane, carbon disulfide, DCM, MIBK, and acetone. On January 14, 2020, the five compounds were spiked simultaneously into a stock of RO permeate at ~1.0 mg/L as C, which corresponds to 3.1 mg/L, 6.4 mg/L, 7.1 mg/L, 1.4 mg/L, and 1.6 mg/L VOC concentrations for 1,2-dichloropropane, carbon disulfide, DCM, MIBK, and acetone, respectively. Immediately upon spiking the spiked solutions were sonicated to help with dissolution of VOC into solution. Then the spiked solutions were transferred to trace-clean VOC vials in triplicate. The transfer time was deliberately performed over 45 minutes to mimic the time it would take for this same step during TOC Performance Evaluation task. VOC samples were prepared for the holding test conditions described in Table A-4.

Table A-4. Test Conditions and VOC Sample Matrix.
Samples were spiked with VOCs and held at the SNWA laboratory and then submitted for analysis for the corresponding holding time to Silver State Analytical Laboratories, Las Vegas (NV), and the SNWA laboratory.

Test Condition	Number of Replicate Samples Analyzed by Silver State	Number of Replicate Samples Analyzed by the SNWA Laboratory
Initial analysis	3	3
Hold 24 hour, 4 °C	3	-
Hold 24 hour, 25 °C	3	-
Hold 7 day, 4 °C	3	3
Hold 7 day, 25 °C	3	-

The initial measurement served as a reference for the Day 1 and 7 measurements. Following the required hold times, the samples were analyzed for VOCs. VOC samples were sent to SS Analytical Laboratories for analysis. SS Analytical Laboratories used a ×100 dilution factor and reporting limits of 500 μg/L for each of the VOCs. Additional duplicate VOC samples were prepared and analyzed in-house by SNWA for analytical verification. Only the initial analysis and holding time of 7 days at 4°C were submitted in-house (SNWA) for VOC analysis. SNWA analyzed only 2 of the 5 VOCs (DCM and 1,2-dichloropropane) since SNWA's method did not have the other VOCs on its method list.

The target concentration was compared against the initial measured concentration to evaluate the analytical matrix spike recovery for the target compounds (Table A-5). The spike matrix recovery criterion was ± 30% for VOC analysis for EPA methods. 1,2-dichloropropane, DCM and MIBK matrix spike recoveries were within this range. It is unknown why the matrix spike recovery for carbon disulfide was high (150%; target concentration = 1.0 mg/L as C), but the recovery was consistently higher with ROP where the recovery was 130% (target concentration = 0.5 mg/L as C) for the TOC Performance Evaluation Study (Table A-9). It is unknown why acetone was not recovered in the initial measured sample; however, it was detected in all the samples held for 7 days. This variability is discussed further in the results section.

Table A-5. Target and Initial VOC Concentrations and Analytical Matrix Spike Recoveries for Preliminary Holding Study #1.
Compounds were spiked as a mixture. Values that are bolded and italicized are outside of the ± 30% recovery criteria.

Compounds	Target Conc. (mg/L as C)	Initial Conc. (mg/L as C)	Recovery (%)
1,2-Dichloropropane	1.00	0.81	81
DCM	1.00	0.92	92
Carbon disulfide	1.00	1.50	***150***
MIBK	1.00	0.87	87
Acetone	1.00	<0.31 (MRL)	-

A.2.7 Inter-laboratory Comparison

Another preliminary holding study with RO permeate was performed in order to compare methods of two analytical laboratories for measuring acetone (potentially lower reporting limit) and adjust the technique for adding the target compounds into the RO permeate (extended the equilibrium time after addition). Each target compound was spiked into RO permeate at 1 mg/L as C on February 12, 2020, and allowed to sit overnight before pouring the solution into vials on February 13, 2020. Note, for the preliminary VOC holding study, the spiking and subsequent transferring of solution occurred on the same day. For ROF, just a holding time of 7 days at 25°C was evaluated. VOC methods by Eurofins Eaton Analytical and SS Analytical Laboratories were compared. SS Analytical Laboratories reported a 200-dilution factor for samples and reporting limits of 1,000 µg/L for each of the VOCs. Eurofins Eaton Analytical reported a 1,000-dilution factor for samples and reporting limits of 500 µg/L, except for MIBK and acetone which had reporting limits of 5,000 and 10,000 µg/L, respectively.

A.2.8 TOC Analyzer Performance Evaluation Approach for ROP and ROF

A.2.8.1 TOC and VOC Experimental Matrices

The objective of this task was to determine if individual VOCs and a mixture of VOCs in RO permeate (ROP) and RO feed (ROF) can be effectively measured by online and bench-top TOC analyzers. ROF was evaluated since this could be another location to employ a TOC analyzer at RO facilities. The VOCs targeted included DCM, acetone, MIBK, carbon disulfide and 1,2-dichloropropane. A total of 6 different TOC instruments from a total of 9 participants were assessed (Tables A-3 and A-6). Testing of the analyzers occurred over two events, as summarized in Tables A-7 and A-8. A concerted effort was made to coordinate sampling schedules of participating laboratories in order to utilize the same VOC stock solution for each sample matrix (ROP and ROF) and minimize variation from preparation and/or storage between new stock solutions. Duplicate TOC samples were shipped to participants, which also included an additional replicate in case of sample breakage.

The instruments were evaluated based on the TOC Performance Recovery, which is the percentage of the measured TOC concentration in a fortified matrix with the background TOC subtracted out relative to the initially measured VOC concentration as carbon in the same matrix. An acceptable recovery is one between 85 and 115%, which is set by SM 5310 for the TOC analysis of a fortified sample.

Table A-6. List of Participants, Their Respective Analyzers, and Their Carbon Measurements.

Participant	Water Type	Method	Model	Bench Top	Online	IC Removal	Measured Carbon Parameter
A	ROP ROF	PUO	Sievers M5310C	-	√	On	TOC/TC/TIC
B	ROP ROF	PUO	Sievers M5310C	-	√	On	TOC/TC/TIC
C	ROP	TSAO	Hach B3500	-	√	On	TOC/TC/TIC
C	ROF	TSAO	Hach B7000	-	√	On	TOC/TC/TIC
D	ROP ROF	PUO	Sievers M9	-	√	On	TOC
D	ROP ROF	PUO	Sievers M5310C	√	-	On	TOC/TC/TIC
D	ROP ROF	PUO	Sievers M5310C	√	-	Off	TOC/TC/TIC
E	ROP ROF	PUO	Sievers M9	-	√	On	TOC/TC/TIC
F	ROP ROF	HTC	Shimadzu TOC-L	√	-	On	TOC
G	ROP ROF	HTC	Shimadzu TOC-L	√	-	On	TOC
G	ROF	HTC	Shimadzu TOC-L	√	-	Off	TC/TIC
H	ROF	HTC	Shimadzu TOC-L	√	-	On	TOC
H	ROF	HTC	Shimadzu TOC-L	√	-	Off	TC/TIC
I	ROF	HTC	Shimadzu TOC-4200	-	√	On	TOC
I	ROF	HTC	Shimadzu TOC-4200	-	√	Off	TC/TIC

Table A-7. Number of TOC Samples Analyzed by Each Participant and Number of VOC Samples Analyzed by Silver State Analytical Laboratories (SS) for ROP.

Sample ID	Spike Level	TOC	Initial VOC*	Holding VOC**
ROP	Ambient	2	2	-
ROP + DCM	0.5 mg/L as C	2	2	-
ROP + Acetone	0.5 mg/L as C	2	2	-
ROP + MIBK	0.5 mg/L as C	2	2	-
ROP + Carbon Disulfide	0.5 mg/L as C	2	2	-
ROP + 1,2-Dichloropropane	0.5 mg/L as C	2	2	-
ROP + Mixture	2 mg/L as C	2	2	1
SST- sucrose	0.5 mg/L as C	2	-	-
SST- 1,4-benzoquinone	0.5 mg/L as C	2	-	-
Reagent water	-	2	-	-

* Submitted by SNWA to SS for initial analysis; **Each participant shipped the VOC mixture samples to SS on the day the TOC was analyzed by the participant to assess any losses during the holding period.

Table A-8. Number of TOC Samples Analyzed by Each Participant and Number of VOC Samples Analyzed by Silver State Analytical Laboratories (SS) for ROF.

Sample ID	Spike Level	TOC	Initial VOC*	VOC 6 days*	VOC 13 days*
ROF	Ambient	2	2	-	-
ROF + DCM	2.0 mg/L as C	2	2	2	2
ROF + Acetone	2.0 mg/L as C	2	2	2	2
ROF + MIBK	2.0 mg/L as C	2	2	2	2
ROF + Carbon Disulfide	2.0 mg/L as C	2	2	2	2
ROF + 1,2-Dichloropropane	2.0 mg/L as C	2	2	2	2
ROF + Mixture	8.0 mg/L as C	2	2	2	2
SST- sucrose	2.0 mg/L as C	2	-	-	-
SST- 1,4-benzoquinone	2.0 mg/L as C	2	-	-	-
Reagent water	-	2	-	-	-

* All samples were submitted to SS by SNWA initially, where the days 6 and 13 samples were held at SS. SS measured VOCs for initial analysis and after 6 and 13 days of holding.
SST – System Suitability Test.

A.2.8.2 VOC Spiking

Spiked solutions were prepared by SNWA in ROP and ROF backgrounds (June 1, 2020, for ROP and July 20, 2020, for ROF). Each sample matrix was prepared as a single stock solution for individual compounds and as a mixture. The spiked concentrations in ROP and ROF backgrounds were 0.5 mg/L and 2 mg/L as C, respectively, for individual compounds, and a total of 2 mg/L and 8 mg/L as C for the compound mixture, respectively. Target and initial VOC concentrations and recoveries are reported in Table A-9. Solutions sat overnight without headspace and transferred the next day into 40 mL sample vials without headspace.

A.2.8.3 Holding Study

For ROP, SNWA sent spiked samples (individual and mixture spiked ROP) for VOC analyses directly to SS. Another portion of samples (mixture spiked ROP) were sent to participating utilities and laboratories for TOC analyses. These participating utilities and laboratories then forwarded a third set of samples (mixture spiked ROP) onward to SS for VOC analyses (Table A-7). VOC shipping losses were calculated as the difference in VOCs between the samples sent directly to SS and the samples sent first to other labs and then onward to SS. VOC contents of ROP and ROF waters were also analyzed by SS to check ambient concentrations of the compounds examined in this study. While ROP had acetone near the detection limit, the concentrations of the target VOC in ROF water were non-detect. For ROP, SS Analytical laboratories reported a 25 times dilution factor for samples and reporting limits of 125 µg/L, except for MIBK and acetone which had reporting limits of 312 µg/L.

For ROF, samples (spiked ROF) for VOC analyses did not travel to participating utilities and laboratories alongside samples (spiked ROF) for TOC analyses. Rather, samples were held at SS at 4 °C and analyzed for VOCs at 0, 6, and 13 days (Table A-8). For ROF, SS Analytical Laboratories reported a 200 times dilution factor for DCM and carbon disulfide and reporting limits of 1000 µg/L; a 100 times dilution factor for 1,2-dichloropropane and a reporting limit of 500 µg/L; and a 50 times dilution factor for MIBK and acetone and reporting limits of 625 µg/L.

The target concentration was compared against the initial measured concentration to evaluate the analytical matrix spike recovery for the target compounds (Table A-9). The spike recovery criteria is ± 30% for VOC analysis for EPA methods. Most of the matrix spike recoveries were within this range. Again, it is unknown why the matrix spike recovery for carbon disulfide in the mixture was high (188%; target concentration = 1.0 mg as C), but this time with ROF. Also, the recovery for MIBK in the mixture for ROP was unexpectedly low (55%).

Table A-9. Target and Initial VOC Concentrations and Analytical Matrix Spike Recoveries for ROP and ROF.
Values that are bolded and italicized are outside the ± 30% recovery criteria.

Compound	ROP Target Conc. (mg/L as C)	ROP Actual Conc. (mg/L as C)	ROP Recovery (%)	ROF Target Conc. (mg/L as C)	ROF Actual Conc. (mg/L as C)	ROF Recovery (%)
Individual Spikes:						
1,2-Dichloropropane	0.50	0.53	106	2.00	2.20	110
DCM	0.50	0.56	112	2.00	2.25	112
Carbon Disulfide	0.50	0.65	130	2.00	2.19	110
MIBK	0.50	0.61	121	2.00	2.63	***131***
Acetone	0.50	0.64	128	2.00	2.50	125
Mixture Spike:						
1,2-Dichloropropane	0.50	0.50	99	2.00	2.13	107
DCM	0.25	0.28	112	1.00	1.10	110
Carbon Disulfide	0.25	0.30	118	1.00	1.88	***188***
MIBK	0.50	0.27	***55***	2.00	1.88	94
Acetone	0.50	0.61	122	2.00	1.82	91

A.2.8.4 System Suitability Tests

TOC instrument system suitability tests (SST) used as an independent quality control check of the participants' TOC instruments were conducted in parallel with ROP and ROF testing to benchmark each TOC instruments' response efficiency. Two separate SSTs were conducted, adapted from US Pharmacopeia (USP) Method 643; one during ROP testing and another during ROF testing (Table A-6). USP Method 643 uses two standard solutions. One is called the Standard Solution, which contains an easy-to-oxidize organic compound (i.e., sucrose), and a System Suitability Standard Solution, which contains a difficult to oxidize organic compound (i.e., 1,4-benzoquinone). SNWA prepared the sucrose and 1,4-benzoquinone solutions with reagent water and they were shipped in triplicate with ROP and ROF TOC samples, respectively, as unidentified QA/QC samples to ensure unbiased analysis. For ROP, an SST was applied using a Standard Solution of 1.19 mg/L of sucrose (0.50 mg/L as C) and a System Suitability Standard Solution of 1,4-benzoquinone of 0.75 mg/L (0.50 mg/L as C). For ROF, the SST was performed using a Standard Solution of 4.75 mg/L of sucrose (2.0 mg/L as C), and a System Suitability Standard Solution of 1,4-benzoquinone of 3.0 mg/L (2.0 mg/L as C). As part of the SSTs and QA/QC, reagent water (i.e., sample blank) was also shipped for analysis. Participants measured the TOC and reported all results for ROP and ROF to SNWA for calculation of the response efficiency and determination of the compound spike recoveries. The USP method follows the following formula for evaluation of the response efficiency:

$$\%\text{ response efficiency} = 100[(r_{SS} - r_W)/(r_S - r_W)]$$

where r_W is the TOC instrument response for reagent water, r_S is the measured TOC concentration of the Standard Solution of sucrose, and r_{SS} is the measured TOC concentration of the System Suitability Standard Solution of 1,4-benzoquinone. The acceptable response efficiency is 85 to 115%. Instruments with response efficiencies above this range would indicate performance outside of expected range, which should be addressed by maintenance and recalibration. As such, the SST provides an independent quality control check of the participants' TOC instruments.

A.2.9 Recovery Calculations

The recovery was calculated to determine the percentage of a compound that was recovered in the following ways:

1. VOC Analytical Matrix Spike Recovery: percentage of the measured VOC concentration in a fortified matrix relative to the target VOC concentration,
2. TOC Analytical Recovery: percentage of the measured TOC concentration of a target organic compound in reagent water relative to the target TOC concentration.
3. VOC Holding Recovery: percentage of the measured VOC concentration in a fortified matrix after a holding period relative to the initially measured VOC concentration in the same matrix.
4. TOC Performance Recovery: percentage of the measured TOC concentration in a fortified matrix (background TOC is subtracted out) relative to the initially measured VOC concentration as carbon in the same matrix.

These recovery definitions and the location of the corresponding recovery data in tables or figures are summarized in Table A-10.

Table A-10. Summary of Recovery Calculations.

Recovery	Recovery Calculation	Criteria	Task	Data Location
VOC Analytical	Initial VOC Conc./ Target Conc. x 100	±30%	Analytical Verification:	Tables A-4 & A-9
VOC Holding	VOC Holding Time Conc./ Initial VOC Conc. x 100	±30%	Preliminary VOC Holding Study #1: VOC Holding:	Figure A-1 Table A-12
TOC Analytical	(TOC Conc. - Background TOC)/ Target Conc. (as C) x 100	±15%	System Suitability Test:	Table A-13
TOC Performance	(TOC Conc. - Background TOC)/ Initial VOC Conc. (as C) x 100	±15%	TOC Performance Evaluation:	Table A-14

A.3 Results and Discussion

A.3.1 Preliminary VOC Holding Study

The VOC holding recovery calculations were based on the initial measured concentrations for each compound. The holding recoveries for DCM, MIBK, 1,2-dichloropropane and carbon disulfide were within or near ± 30% and relatively stable during the 7 days at both 5 and 25°C (Figure A-1C). Thus, temperature had minimal impact for these VOCs up to 7 days. The precision was high for these compounds with the RSD typically < 6% (Figure A-1B). The measured concentrations for DCM and 1,2-dichloropropane were comparable between SS and SNWA laboratories (Table A-11) for initial and Day 7 samples at 4°C demonstrating analytical reproducibility in the measurements for these two compounds.

The carbon disulfide, DCM, and 1,2-dichloropropane concentrations increased from the initial to Day 1 sample (Figure A-1A), which resulted in higher holding recoveries. This and the visible observation of a precipitate on day 0 (initial) led to concern that when the initial spiked solution was sampled, it was not completely mixed or the compounds were not completely dissolved leading to the lower initial concentrations.

Interestingly, acetone was not detected in the initial triplicate samples (< 500 ppb) (Table A-4; Figure A-1A). Note, the acetone recovery data in Figure A-1D is based on the calculated target concentration of acetone and not the initial concentration. For the triplicate Day 1 samples for both 5 and 25°C conditions, acetone concentration was below the MRL (< 500 ppb) for two of the replicates but was detected in the remaining replicate, but it was detected 6 to 10 times higher than the MRL. However, acetone was detected in all triplicate samples for Day 7 samples for both 5 and 25°C conditions, though the RSD was > 5% (Figure A-1B). Interestingly, the Day 7, 25°C, sample recovery was within the ± 15% criteria when using the target acetone concentration as the comparison. Given the acetone replicate concentrations were highly variable and low initial measured concentrations for some of the VOCs, a follow up study was decided to be performed to evaluate a longer mixing/equilibrium time and compare measurements with another analytical laboratory, Eurofins Analytical, for the analysis of acetone.

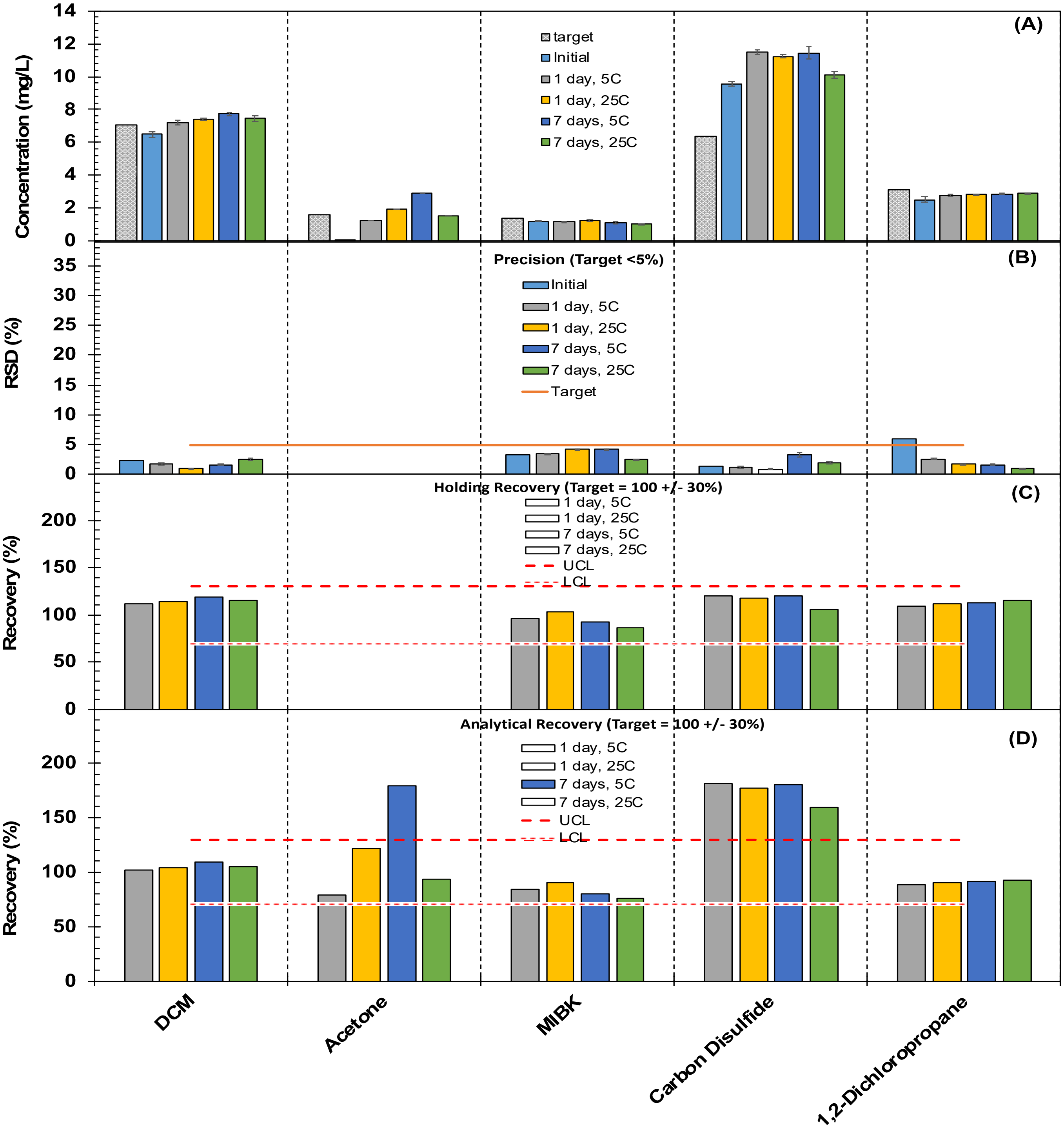

Figure A-1. The VOC Concentration, Precision, and Holding Recovery Results for Holding Study.
C: VOC holding recoveries were calculated based on the initial measured concentration. D: VOC analytical recoveries were calculated based on the target concentration.

Table A-11. Comparison of VOC Analytical Recoveries Measured by SS Analytical and SNWA Laboratories for Preliminary Holding Study (7 Days at 4°C).

VOC	Target (mg/L)	SNWA Initial (mg/L)	SS Initial (mg/L)	SNWA Day 7 (mg/L)	SS Day 7 (mg/L)
DCM	7.08	6.74±0.4	6.48±0.2	8.3±0.8	7.73±0.2
DCM % Recoveries*	-	(95%)	(92%)	(113%)	(109%)
1,2-Dichloropropane	3.14	2.81±0.2	2.53±0.2	3.4±0.2	2.92±0.1
1,2-Dichloropropane % Recoveries *	-	(89%)	(81%)	(105%)	(93%)

*Recoveries were calculated based on the initial target concentration

A.3.2 Inter-laboratory Comparison

Figures A-2A, A-2B and A-2C include the VOC concentration, precision, and VOC analytical matrix spike recovery results, respectively. The recoveries in Figure A-2C were based on the calculated target concentrations of 1 mg/L TOC as C for each compound, since the initial concentrations were not measured for ROF. Given this, DCM, MIBK and 1,2-dichloropropane still had acceptable recoveries (± 30%) for the SS data, whereas carbon disulfide and acetone recoveries were outside of ± 30% for the SS data (Figure A-2C). It is assumed the recoveries would have been better if they were compared against the initial measured levels such as for the preliminary VOC holding study (Figure A-1C).

DCM and 1,2-dichloropropane had better recoveries for the SS data as compared to the Eurofins data (Figure A-2C). Interestingly, the carbon disulfide concentration measured by Eurofins was lower than the target concentration, whereas it was again higher (compared to the preliminary VOC holding study) for the SS data as compared to the target concentration (Figure A-2A). This could be due to variable levels in analytical standards used by each of the laboratories, where carbon disulfide is the most volatile and perhaps could more easily volatilize out of standards. Both labs were able to measure acetone comparably, though they were higher than the calculated target concentration (Figure A-2A). Given the SS data had better precision (Figure A-2B) and Day 7 recoveries for DCM, MIBK, and 1,2-dichloropropane (when using the calculated target concentrations) (Figure A-2C), and SS Analytical Laboratories had good precision for MIBK, DCM, carbon disulfide, and 1,2-dichloropropane for both the preliminary VOC holding study (Figure A-1B) and the inter-laboratory comparison and acetone in the inter-laboratory comparison (Figure A-2B), then it was decided to move forward solely with SS Analytical Laboratories for the TOC instrument performance evaluations.

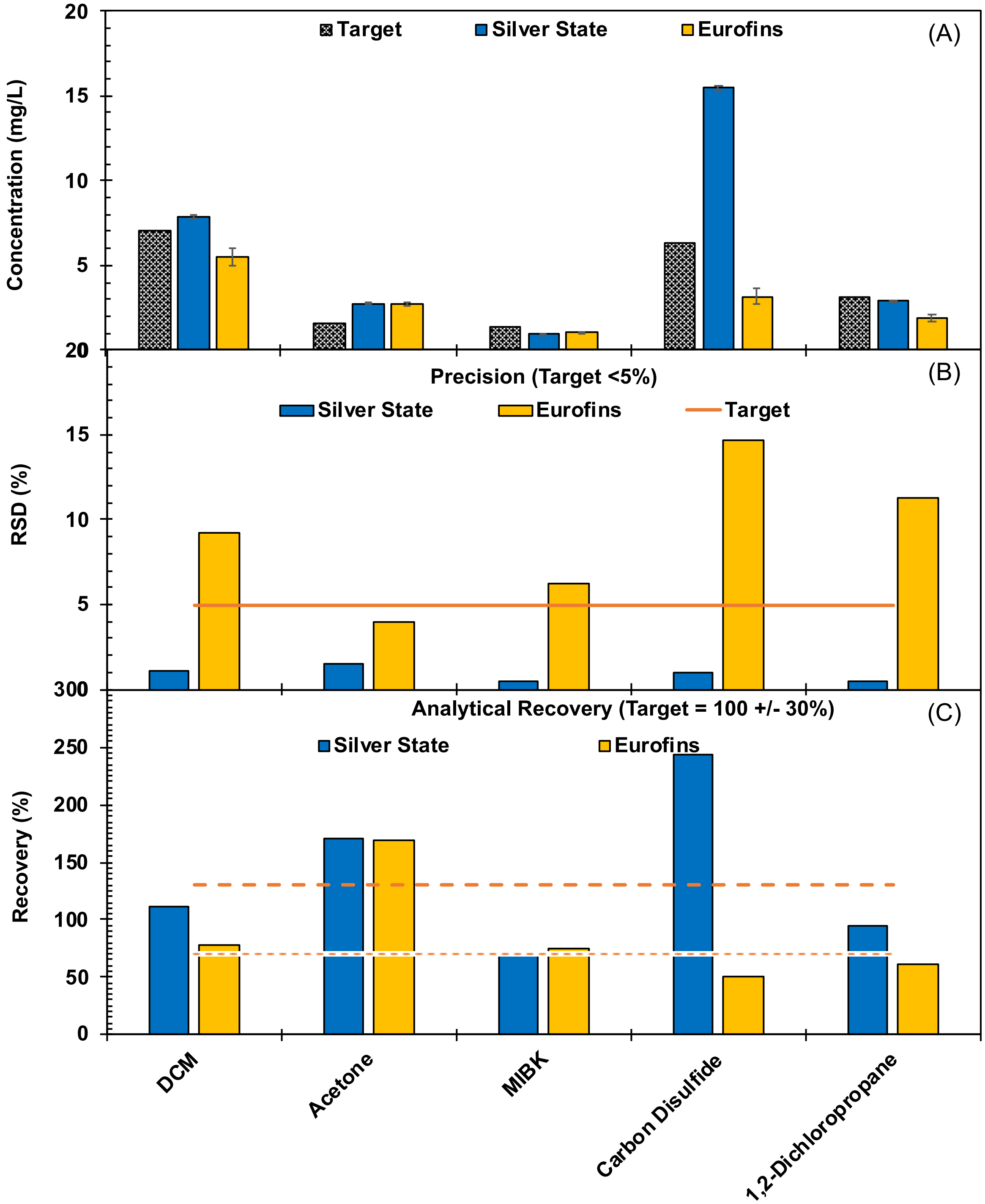

Figure A-2. The Concentration, Precision, and VOC Analytical Recovery Results for the Inter-laboratory Comparison.

VOC Analytical recoveries in Figure A-2C are based on the calculated target concentrations for each compound since the initial concentration values were not measured.

A.3.3 TOC Analyzer Performance Evaluation

A.3.3.1 VOC Holding Recoveries

Similar to the preliminary VOC holding study, the VOC holding recoveries in individual and mixture spikes were calculated based on the initial measured VOC concentrations for both TOC Performance Evaluation for ROP and ROF (Table A-12). The holding recoveries for acetone, DCM, MIBK, 1,2-dichloropropane, and carbon disulfide were within ± 30% and thus relatively stable during the holding periods. The precision was high for these compounds in ROF with a relative percent difference (RPD) <5% (Table A-12). Precision was not quantifiable for ROP, since only one replicate was measured. Exceptions included a high holding recovery of 174% for acetone in the mixture standard for participant B in ROP. Carbon disulfide had low holding recoveries after 6 (59%) days for ROF. In addition, holding recoveries for MIBK were not reportable for most of the sites for ROP (except for site G). This was likely due to the MIBK levels being slightly below the MRL. For example, the MIBK concentration for site G for ROP was 317 µg/L after 3 days, near the MRL of 312 µg/L. Overall the holding recovery results for ROP and ROF indicate minimal loss of the VOCs during transport to participating sites.

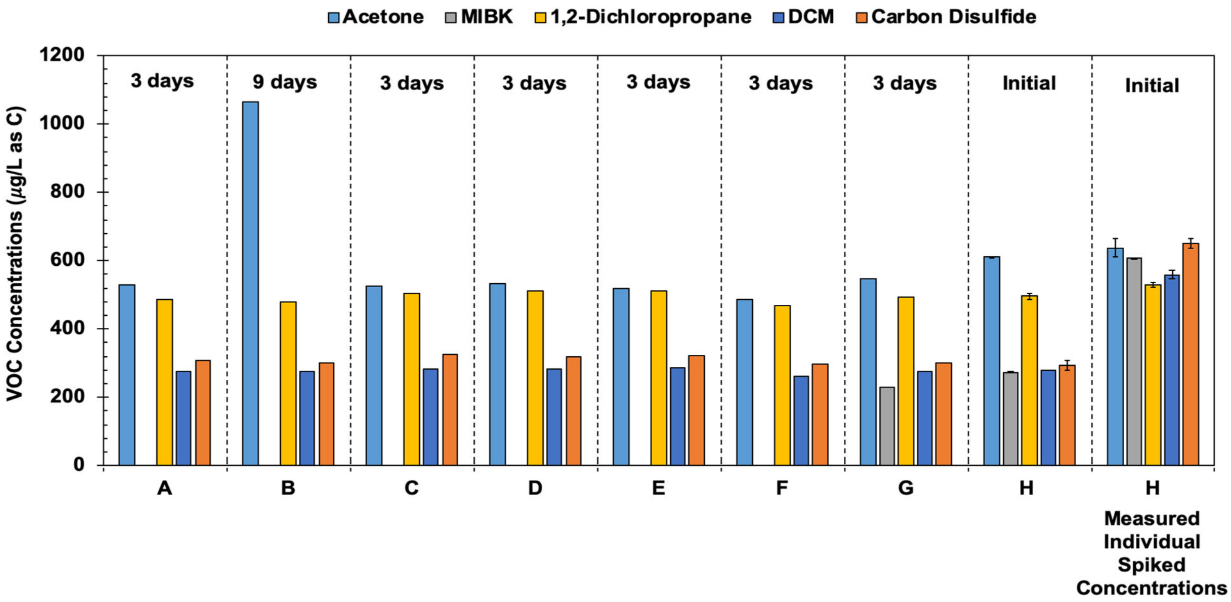

Figure A-3. VOC Concentrations for the VOC Mixture Sample That Was Held and Then Submitted by Participants for ROP.

VOC mixture samples traveled from SNWA (site H) to participating sites and then were shipped by each participant to SS. Initial VOC concentrations from the individually spiked samples are presented as well as a reference.

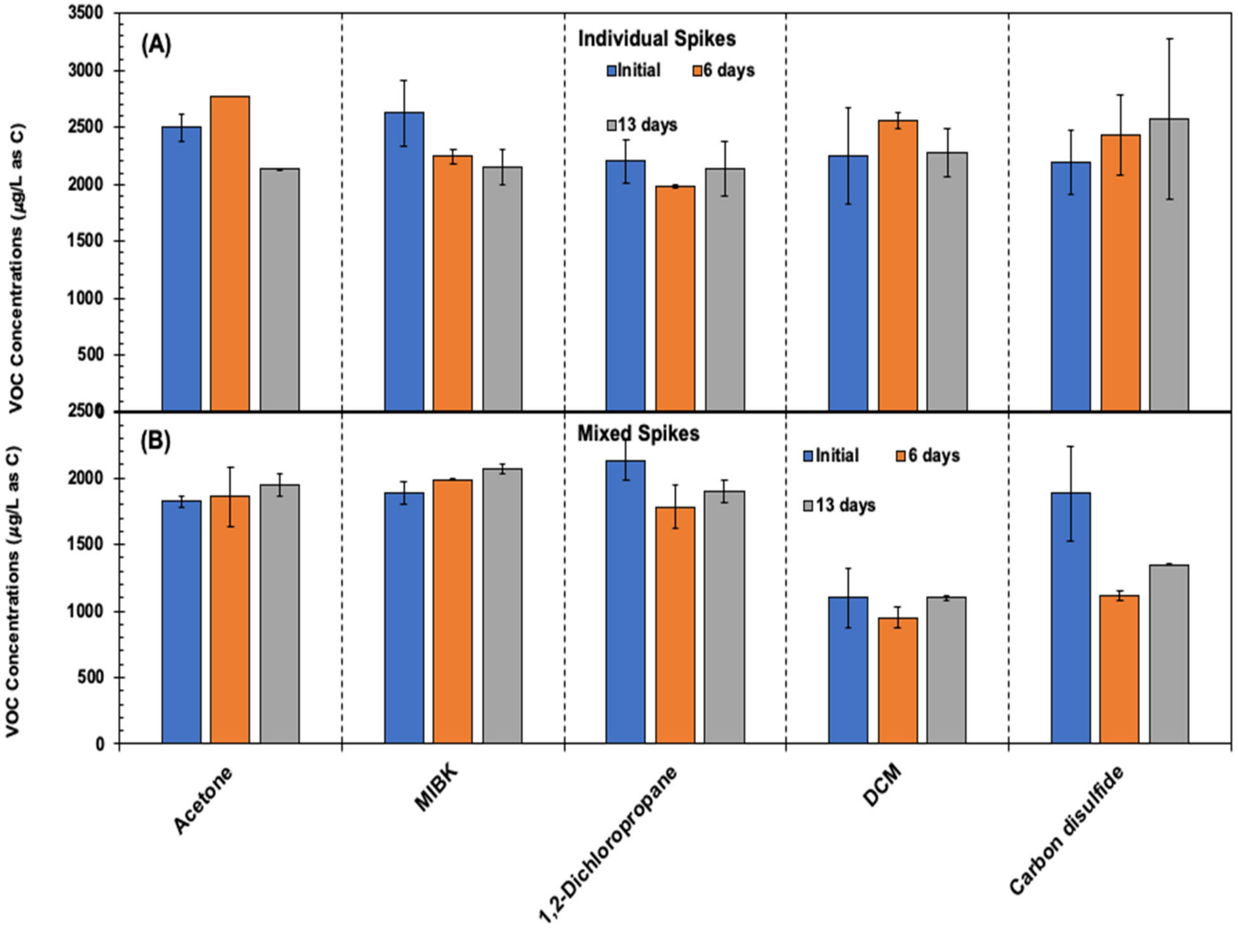

Figure A-4. VOC Concentrations from the Holding Samples in ROF.
VOC holding samples were only submitted by SNWA to SS Analytical Laboratories to test differing holding times.

Table A-12. VOC Holding Recoveries for TOC Performance Evaluations.
Values that are bolded and italicized are outside the ± 30% recovery criteria.

Testing	Participant Recoveries (%)	Holding Times	Acetone	MIBK	1,2-Dichloropropane	DCM	Carbon Disulfide
ROP	**A (Mixture)**	**3 days**	87	NA	98	98	105
ROP	**B (Mixture)**	**9 days**	***174***	NA	97	98	102
ROP	**C (Mixture)**	**3 days**	86	NA	101	101	111
ROP	**D (Mixture)**	**3 days**	87	NA	103	101	108
ROP	**E (Mixture)**	**3 days**	85	NA	103	102	109
ROP	**F (Mixture)**	**3 days**	80	NA	94	94	101
ROP	**G (Mixture)**	**3 days**	90	83	99	99	102
ROF	**H (Individual)**	**6 days**	111±0	85±2	90±0.2	114±0.4	111±3
ROF	**H (Individual)**	**13 days**	85±0.2	82±4	97±4	102±1	117±5
ROF	**H (Mixture)**	**6 days**	102±8	106±0.3	84±2	86±1	***59±0.3***
ROF	**H (Mixture)**	**13 days**	107±3	110±1	89±1	100±0.2	72±0.1

NA: Not Available where values were below and likely near the detection limit. Therefore, an accurate recovery could not be calculated.

A.3.3.2 TOC Performance Recoveries

The summary of TOC performance recoveries is presented in Tables A-13 and A-14. For ROP and ROF, the compound TOC performance recoveries were calculated based on the measured TOC, with the background TOC in the ROP and ROF subtracted out, divided by the initial VOC measured concentrations (as C). The TOC concentration results in background waters for ROP (Average ROP = 151±47 µg/L as C) and ROF (Average ROF = 6716±506 µg/L as C) are presented in Figures A-5 and A-6, respectively. The TOC performance recovery results are organized by the following TOC instrument groupings: online analyzers with IC removal (ICR) [complete (HTC and TSAO) or partial (PUO)], online analyzers with ICR off (HTC), bench-top analyzers with ICR [complete (HTC) or partial (PUO)] and bench-top analyzers with no ICR (HTC and PUO).

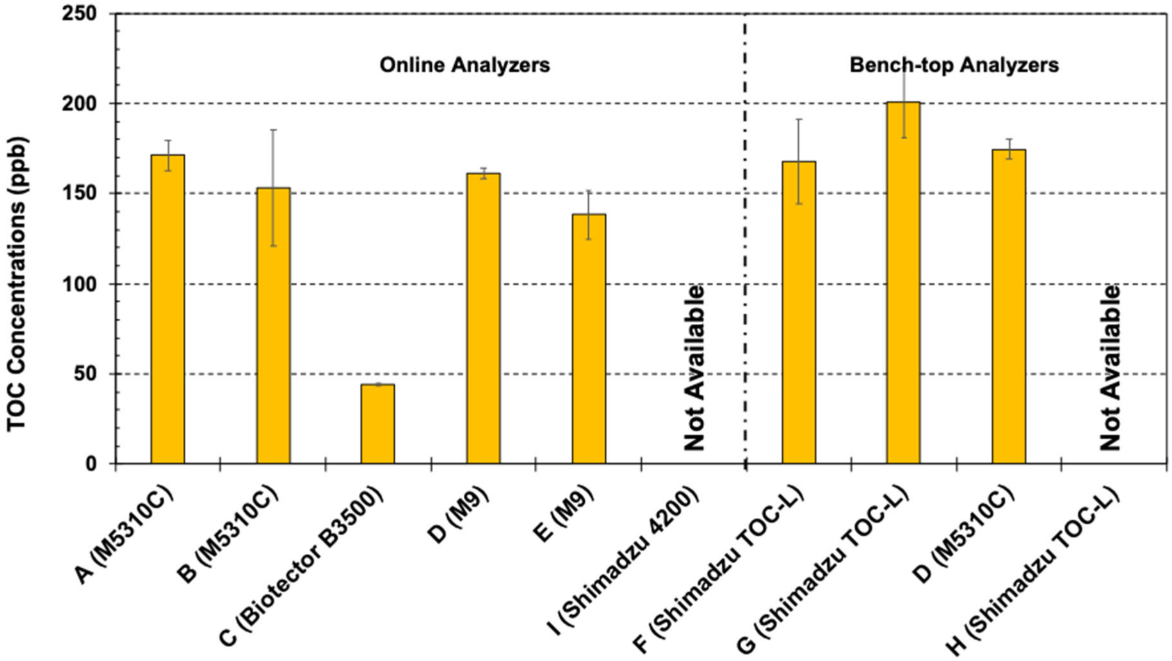

Figure A-5. The Average Measured Concentration of TOC in ROP by Each Participant.
Split samples were shipped to participants from SNWA.

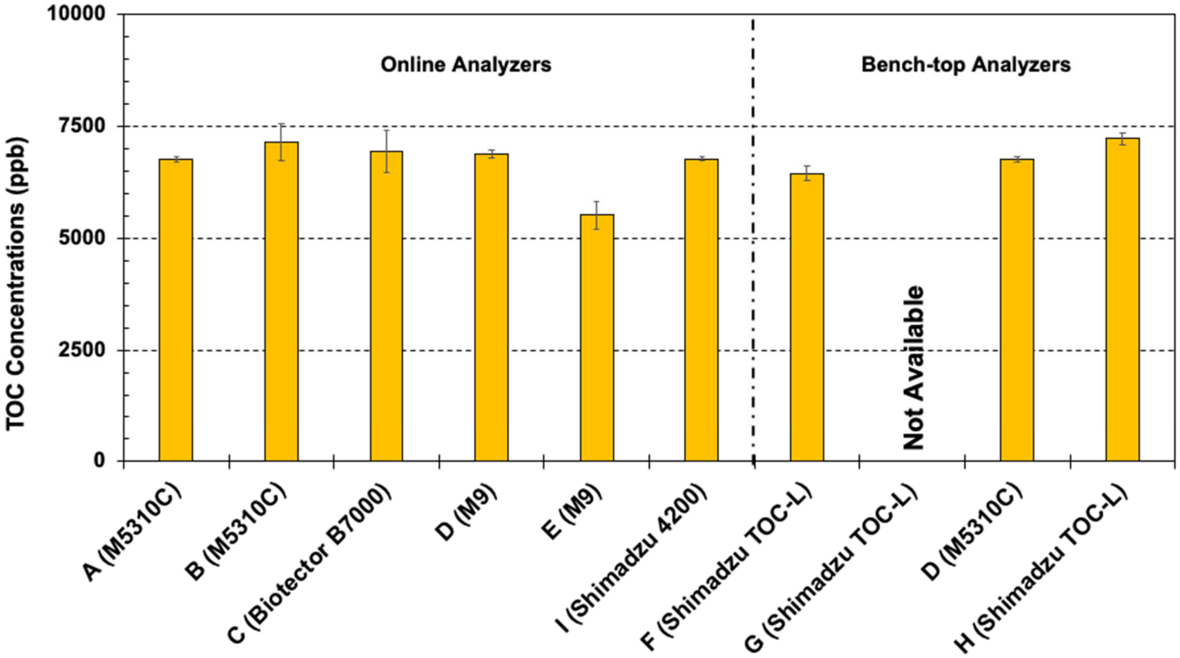

Figure A-6. The Average Measured Concentration of TOC in ROF by Each Participant.
Split samples were shipped to participants from SNWA.

System Suitability Tests

The results of SST testing for ROP are shown in Figures A-7 and A-8 and Table A-13. The calculated response efficiency values in ROP ranged between 71-96% for the tested online and bench-top (ICR-On/Off) analyzers. However, most of the response efficiency values (105-142%) were within 85-115% demonstrating good performance with the exception of two instruments with ICR-On for ROP. Sites C (Biotector B3500) (129%) and G (Shimadzu TOC-L) (142%) demonstrated performance above the acceptable analytical variability (85-115%). The calculated response efficiency values in ROF ranged between 93-105% for the tested online and bench-top (ICR-On/Off) analyzers. These analyzers demonstrated good performance within the acceptable analytical variability (85-115%).

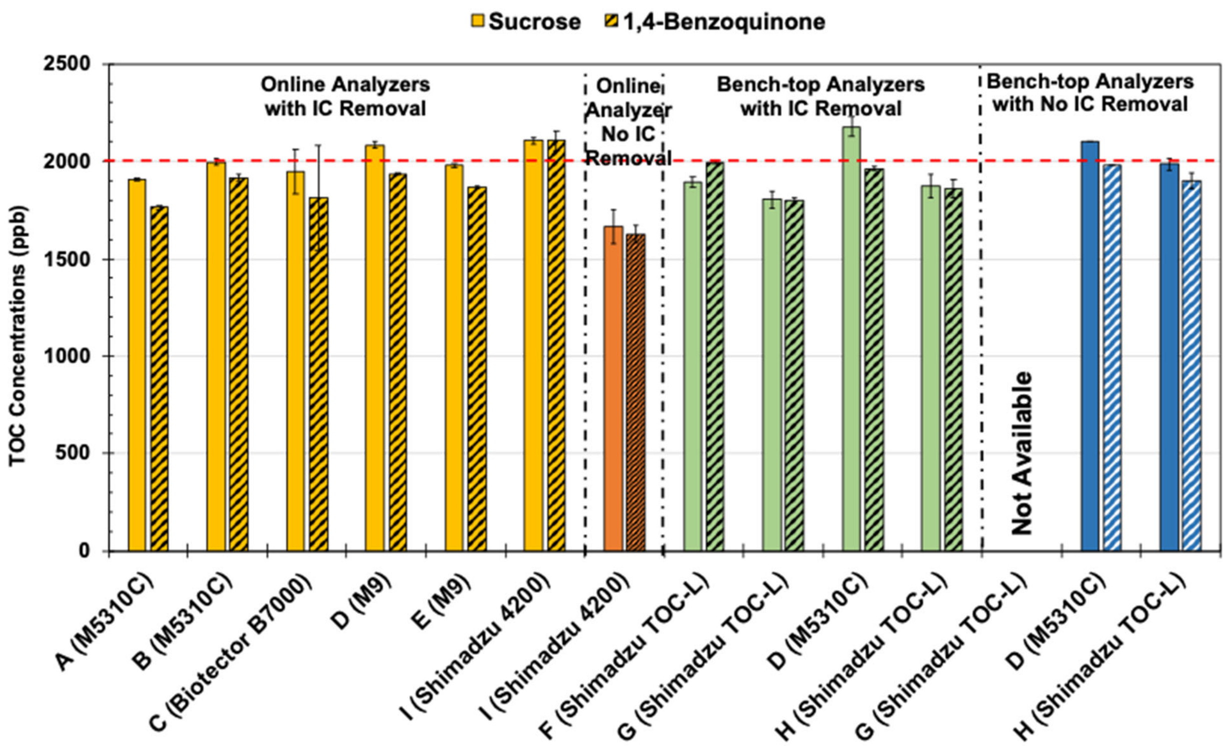

Figure A-7. TOC Concentrations for the System Suitability Testing for ROP.

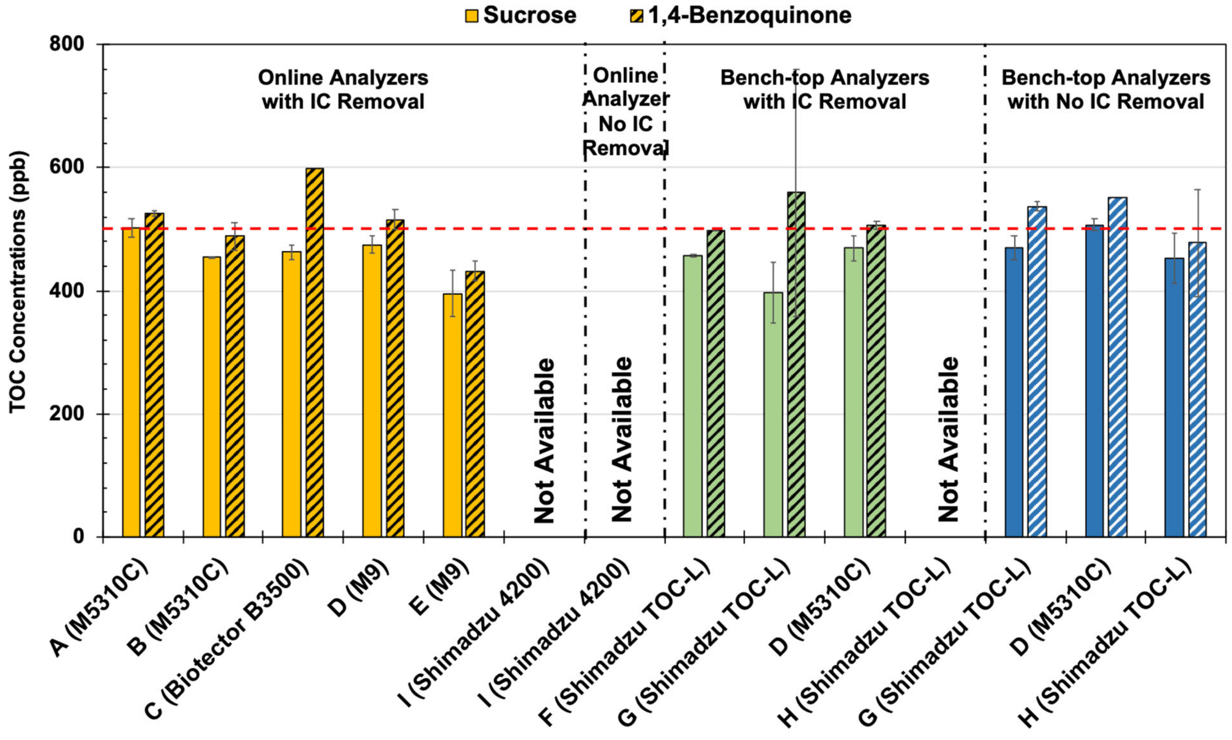

Figure A-8. TOC Concentrations for the System Suitability Testing for ROF.

Table A-13. TOC Analytical Recoveries and Response Efficiencies for Samples Spiked with SST Compounds.

Values that are bolded and italicized are outside of the ± 15% efficiency criteria.

Participants	1,4-Benzoquinone Recovery (%) ROP	Sucrose Recovery (%) ROP	Calculated Response Efficiency (%) ROP	1,4-Benzoquinone Recovery (%) ROF	Sucrose Recovery (%) ROF	Calculated Response Efficiency (%) ROF
A (M5310C)	105±1	100±3	105	88±1	95±0.5	93
B (M5310C)	98±5	91±0.4	108	96±1	100±0.8	96
C (Biotector B3500)	120±NA	93±2	***129***	NA	NA	NA
C (Biotector B7000)	NA	NA	NA	91±13	97±5.7	94
D (M9)	103±3	95±3	108	97±0.3	104±0.9	93
E (M9)	86±3	79±8	109	93±0.5	99±0.5	94
I (Shimadzu 4200)	NA	NA	NA	105±2	105±0.8	100
I (Shimadzu 4200)	NA	NA	NA	81±2	83±4.4	98
D (M5310C)	101±1	94±4	107	98±1	109±3	90
F (Shimadzu TOC-L)	100±0.2	91±0.4	110	100±0.3	95±1	105
G (Shimadzu TOC-L)	112±40	79±10	***142***	90±1	90±2	100
H (Shimadzu TOC-L)	NA	NA	NA	93±3	94±3	99
D (M5310C)	110±3	101±2	109	99±0	105±0	94
G (Shimadzu TOC-L)	107±2	94±4	114	NA	NA	NA
H (Shimadzu TOC-L)	95±17	90±8	106	95±2	99±2	96

Online Analyzers/ICR-On	🟪
Online Analyzers/ICR-Off	🟥
Bench-top Analyzers/ICR-On	🟧
Bench-top Analyzers/ICR-Off	🟦

Acetone

Recoveries for acetone in ROP from high to low followed the following order for the online analyzers: D (M9) (81%) ≌ A (M5310C) (79%) > E (M9) (74%) > C (Biotector B3500) (71%). Interestingly, the online analyzer B (M5310C) (53%) did not perform as well as its online analog A (M5310C). The TOC recovery data, 79%, for the online instrument A (M5310C) agreed with its bench-top analogs with ICR, D (M5310C) (78%), and without ICR, D (M5310C) (81%). Among the tested analyzers, the bench-top analyzer at site G (Shimadzu-TOC-L) with ICR exhibited the highest TOC recovery, 93% (but low precision of ±15%) while it had the lowest recovery when ICR was off on the same analyzer.

In ROF, the TOC recoveries for online analyzers followed the order of A (M5310C) (87%) > D (M9) (81%) ≌ I (Shimadzu 4200) (79%). B (M5310C) (37%) and E (M9) (49%) analyzers had significantly lower recoveries as compared to their bench-top analogues. The TOC recovery data, 79%, for the online instrument I (Shimadzu 4200) with ICR agreed with its bench-top analogs with ICR (Avg. 74%) [F & G (Shimadzu TOC-L)]. However higher recovery, 88%, was observed for the online instrument I (Shimadzu 4200) with ICR off, suggesting that the ICR process may have purged some acetone for instrument I (Shimadzu 4200).

The bench-top Shimadzu TOC-L with ICR-On (participants F, G, and H) varied in calculated recovery values for ROP (56-93%) and ROF (70-104%). This variability could be due to differing conditions for purging (i.e., rate, time) that impacted the VOC removal. Also, for ROP and ROF the bench-top Shimadzu TOC-L with ICR-Off (participants G and H) had low precision (outside ± 15%) for calculated recovery values. This is likely due to the magnification of RSD in differences when subtracting variables (e.g., TC and IC), especially if the variables are close to each other.

Table A-14. TOC Performance Recoveries for Samples Spiked Individually and as Mixture with VOCs.

Values that are bolded and italicized are outside the ± 15% recovery criteria.

Participants	Acetone ROP	Acetone ROF	MIBK ROP	MIBK ROF	Dichloro propane ROP	Dichloro propane ROF	DCM ROP	DCM ROF	Carbon Disulfide ROP	Carbon Disulfide ROF	Mixture ROP	Mixture ROF
A (M5310C)	***79±2***	87±3	***83±0.5***	***76±2***	***77±5***	***74±8***	***55±2***	***54±2***	***5±2***	***3±2***	***71±0.4***	***70±2***
B (M5310C)	***53±3***	***37±8***	***58±0.3***	***34±10***	***56±4***	***36±5***	***82±2***	***50±3***	***31±22***	***3±4***	***74±0.3***	***28±2***
C (Biotector B3500)	***71±4***	NA	***48±2***	NA	***5±4***	NA	***3±0.2***	NA	***2±3***	NA	***24±5.1***	NA
C (Biotector B7000)	***NA***	***57±5***	NA	***17±5***	NA	ND	NA	ND	NA	NA	NA	***25±6***
D (M9)	***81±3***	***81±1***	87±0.5	***73±1***	***84±2***	***75±4***	***59±2***	***56±0.3***	***2±1***	***1±0.4***	***72±2***	***66±1.3***
E (M9)	***74±0.5***	***49±4***	***78±2***	***46±4***	***72±5***	***61±3***	***54±2***	***64±3***	***3±1***	***21±4***	***65±2***	***44±1.2***
I (Shimadzu 4200)	NA	***79±4***	NA	***50±3***	NA	***6±4***	NA	ND	NA	1***±0.2***	NA	***37±1***
I (Shimadzu 4200)	NA	88±6	NA	87±3	NA	84±19	NA	***71±19***	NA	***36±3.1***	NA	91±6
A (M5310C)	NA	NA	NA	NA	NA	NA	NA	NA	***57±6***	***17±4***	***71±0.5***	85±0.5
D (M5310C)												
F (Shimadzu TOC-L)												
H (Shimadzu TOC-L)	NA	104±9	NA	***76±9***	NA	***8±5***	NA	***19±4***	NA	***2±1***	NA	***43±2***
D (M5310C)	***81±1***	***80±4***	86±2	***76±4***	98±8	89±5	87±1	***74±10***	***64±2***	***42±1***	89±1.5	***77±3***
G (Shimadzu TOC-L)	***28±24***	NA	***35±16***	NA	108±14	NA	***21±14***	NA	***10±16***	NA	***63±15.2***	NA
H (Shimadzu TOC-L)	***30±16***	***160±44***	***35±19***	***125±28***	***39±2***	87±28	***4±11***	***124±67***	ND	***41±6***	***53±6.9***	***79±6***

Online Analyzers/ICR-On	🟪
Online Analyzers/ICR-Off	🟥
Bench-top Analyzers/ICR-On	🟧
Bench-top Analyzers/ICR-Off	🟦

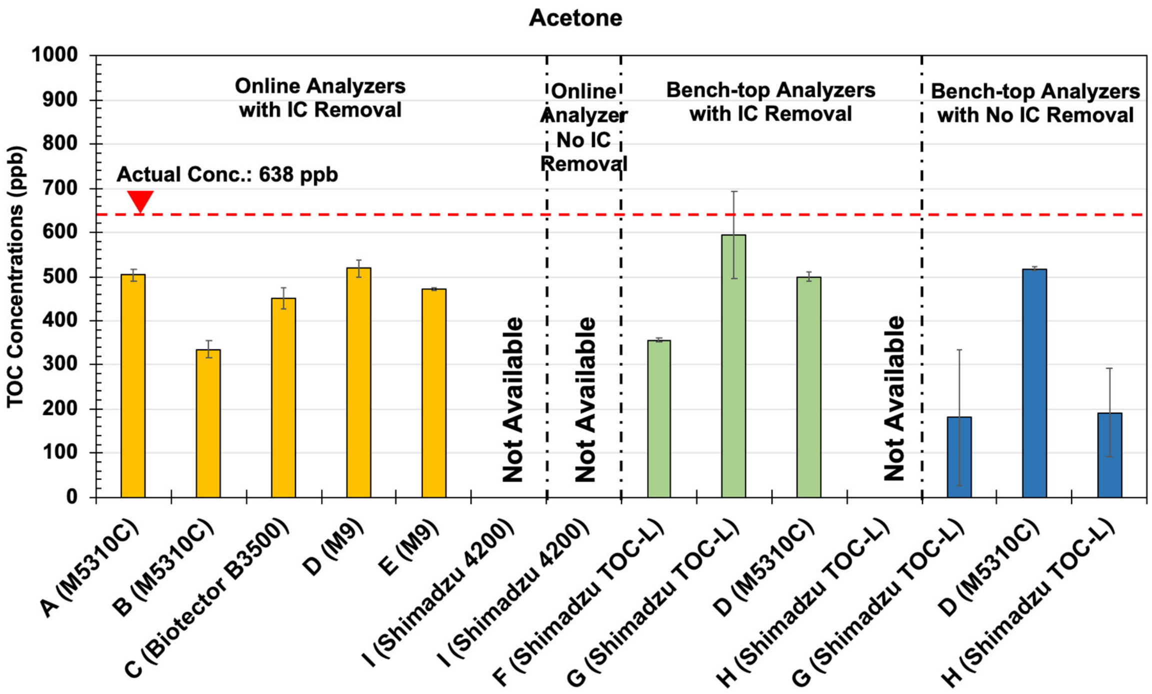

Figure A-9. Measured Acetone TOC Concentrations for ROP.

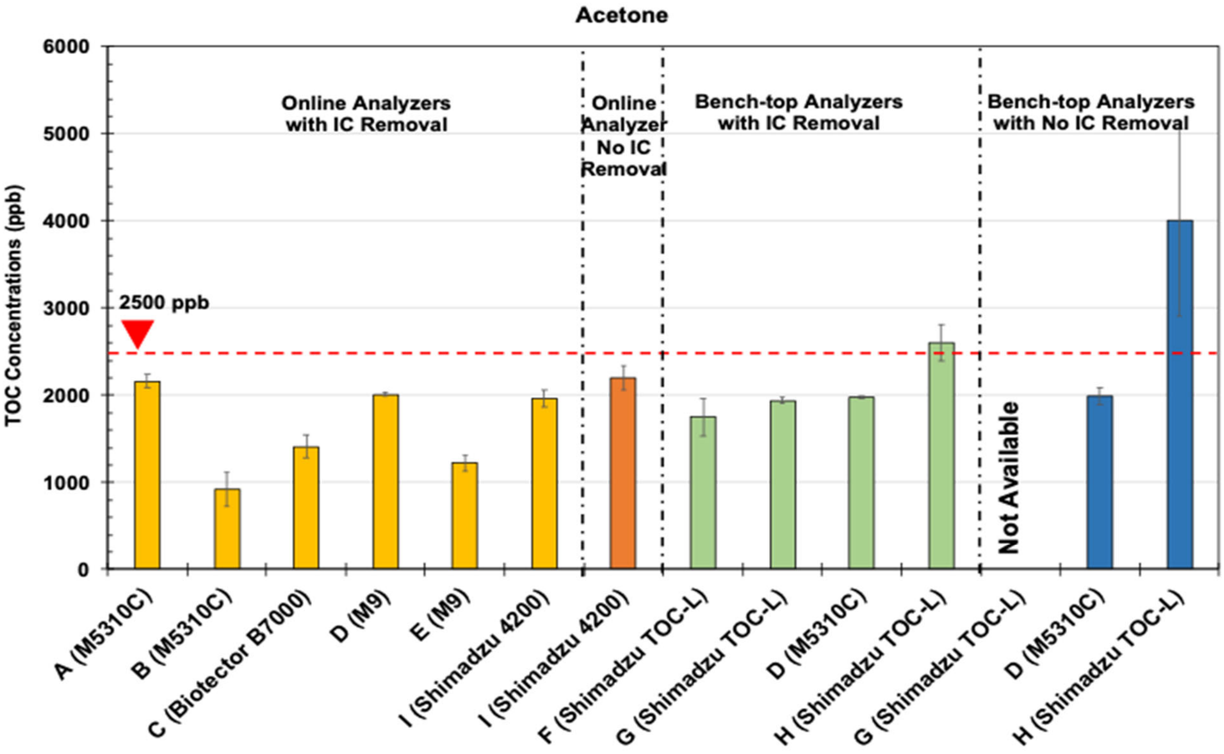

Figure A-10. Measured Acetone TOC Concentrations for ROF.

MIBK

Recoveries for MIBK in ROP from high to low corresponded to the following order for the online analyzers: D (M9) (87%) > A (M5310C) (83%) > C (Biotector B3500) (48%). Similar to acetone, online analyzers B (M5310C) (58%) and E (M9) (78%) did not perform as well as their bench-top analogs A (M5310C) and D (M9), respectively. C (Biotector B3500) did not recover MIBK as well as acetone even though the compounds have similar H_{yc}. The TOC recovery data, 83%, for the online instrument A (M5310C) with ICR agreed with its bench-top analogs with ICR (82%) and without ICR (86%) [D (M5310C)].

Recoveries for MIBK in ROF from high to low corresponded to the following order for the online analyzers: A (M5310C) (76%) > D (M9) (73%) > I (Shimadzu 4200) (50%) ≊ E (M9) (46%) > C (Biotector B7000) (17%). Similar to ROP, C (Biotector B7000) and I (Shimadzu 4200) did not recover MIBK as well as acetone even though the compounds have similar H_{yc}. The TOC recovery data, 50%, for the online instrument I (Shimadzu 4200) agreed with its bench-top analogs with no IC removal (56%) [G (Shimadzu TOC-L)]. However higher recovery, 87%, was observed for the online instrument I (Shimadzu 4200) with ICR off, suggesting that the ICR process may have purged some MIBK for instrument I (Shimadzu 4200).

Similar to acetone results, the bench-top Shimadzu TOC-L with ICR-On (participants F, G, and H) varied in calculated recovery values for ROP (29-75%) and ROF (29-76%). This variability could be due to differing conditions for purging (i.e., rate, time) that impacted the VOC removal. Also, for ROP and ROF the bench-top Shimadzu TOC-L with ICR-Off (participants G and H) had low precision (outside ± 15%) for calculated recovery values. Again, this is likely due to the magnification of RSD in the difference when subtracting variables.

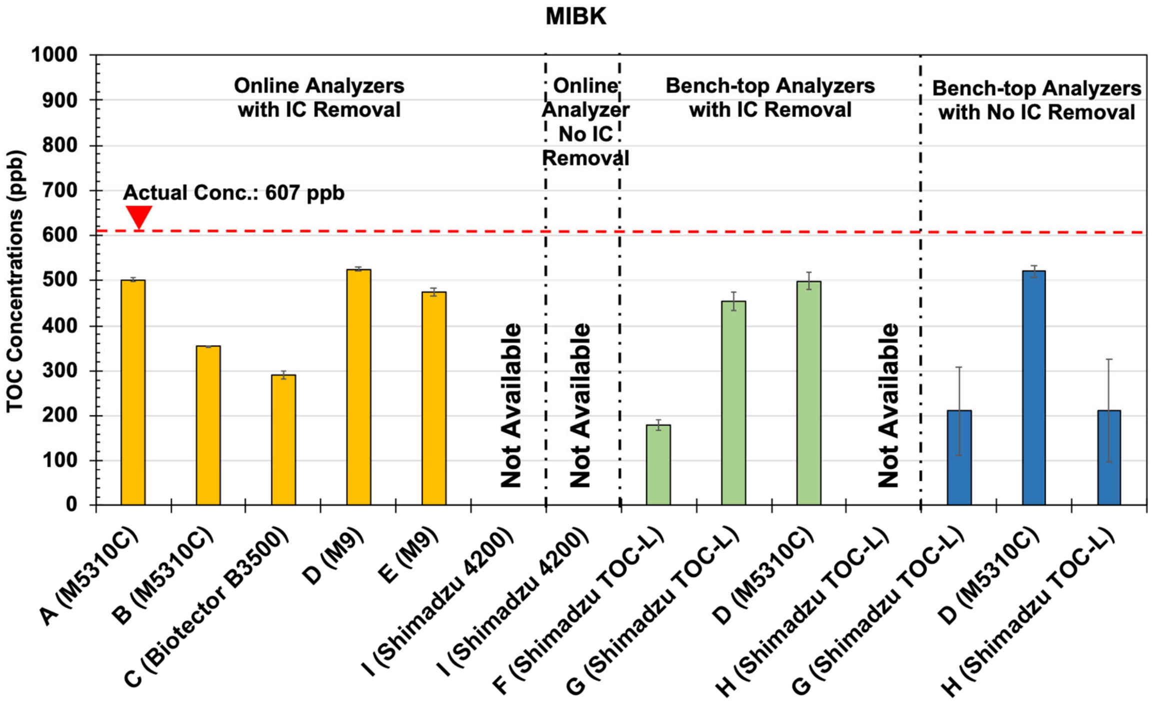

Figure A-11. Measured MIBK TOC Concentrations for ROP.

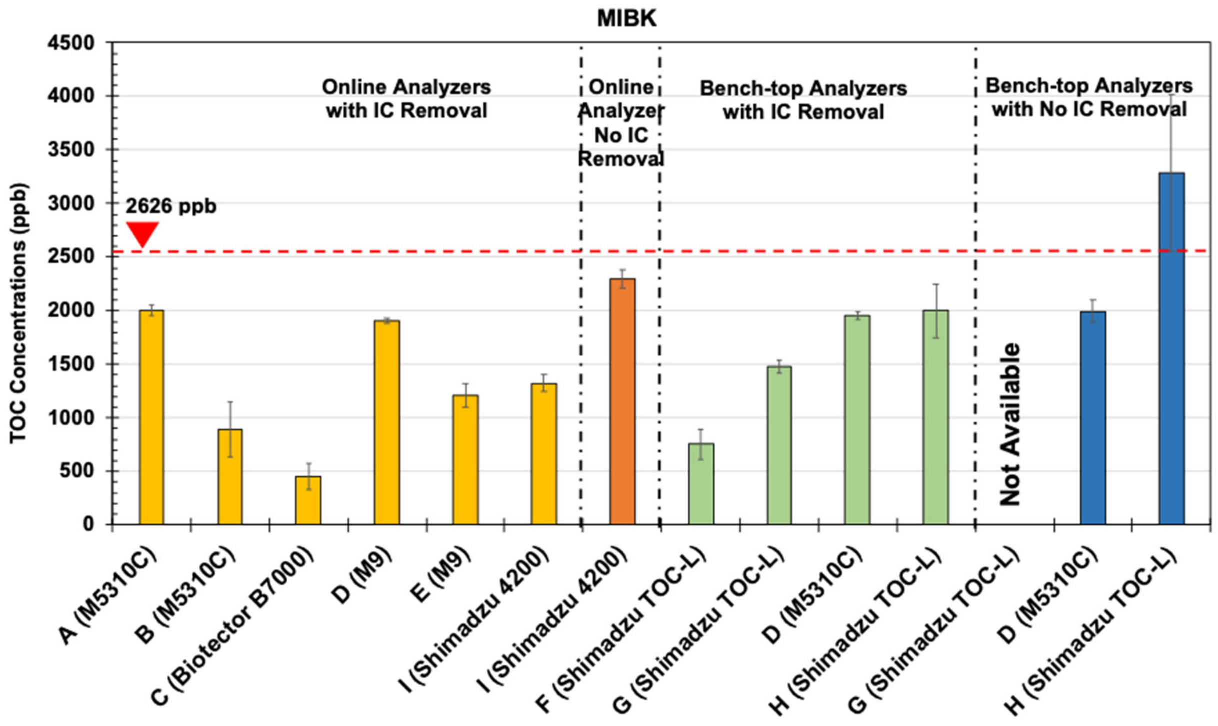

Figure A-12. Measured MIBK TOC Concentrations for ROF.

1,2-Dichloropropane

Recoveries for 1,2-dichloropropane in ROP from high to low corresponded to the following order for the online analyzers: D (M9) (84%) > A (M5310C) (77%) >>> C (Biotector B3500) (5%). Similar to acetone and MIBK, online analyzers B (M5310C) (56%) and E (M9) (72%) did not perform as well as their analogs A (M5310C) (77%) and D (M9) (84%), respectively. C (Biotector B3500) had a poor recovery for 1,2-dichloropropane. It appears this compound was removed during the ICR process of the Biotector instrument. 1,2-dichloropropane is more volatile than acetone or MIBK and poor recovery was also observed for the bench-top Shimadzu instruments with ICR (G and H) (Avg. 8%). However, better recovery was observed with the bench-top Shimadzu instrument (H) with no ICR (39%). The TOC data for the online instrument A (M5310C) (77%) agreed with its bench-top analog, D (M5310C), with ICR (75%). However, the TOC recovery for D(M5310C), 98%, was higher with no ICR indicating the ICR processes for M5310C and M9 instruments are removing some 1,2-dichloropropane.

Recoveries for 1,2-dichloropropane in ROF from high to low corresponded to the following order for the online analyzers: D (M9) (75%) ≃ A (M5310C) (74%) >>> I (Shimadzu 4200) (6%) > C (Biotector B7000) (0%). C (Biotector B7000) and I (Shimadzu 4200) with ICR had poor recoveries for 1,2-dichloropropane. However higher recovery, 84%, was observed for the online instrument I (Shimadzu 4200) with ICR off, suggesting the ICR process purged 1,2-dichloropropane for instrument I (Shimadzu 4200). Thus, it appears this compound was also removed during the ICR process of the Biotector instruments.

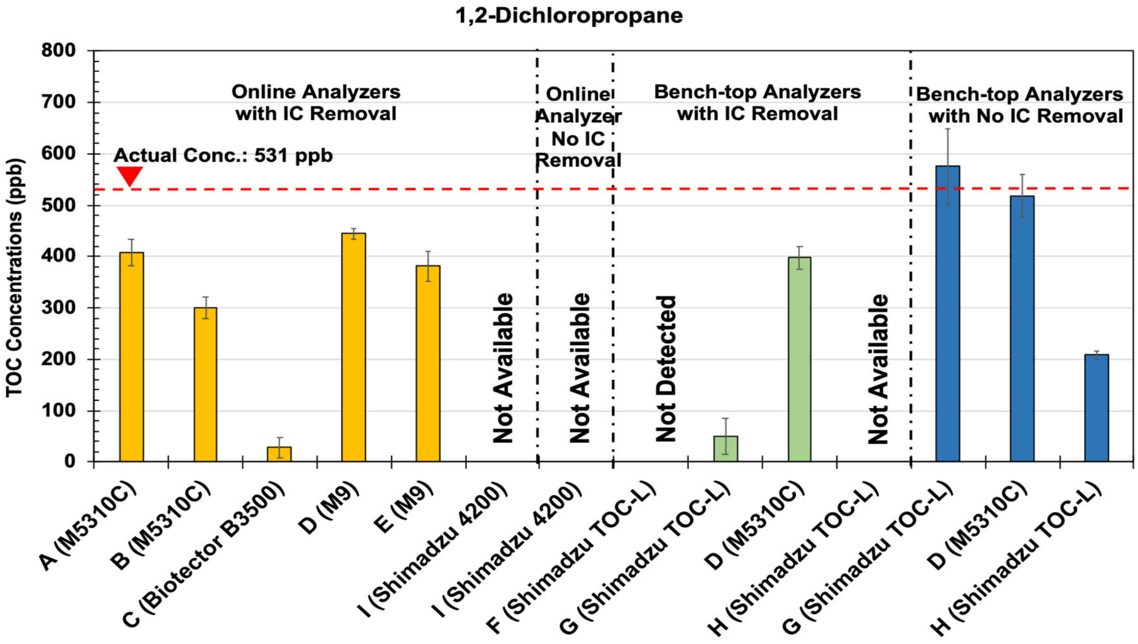

Figure A-13. Measured 1,2-Dichloropropane TOC Concentrations for ROP.
Not Detected: The background concentration was the same or higher than the fortified sample concentration.

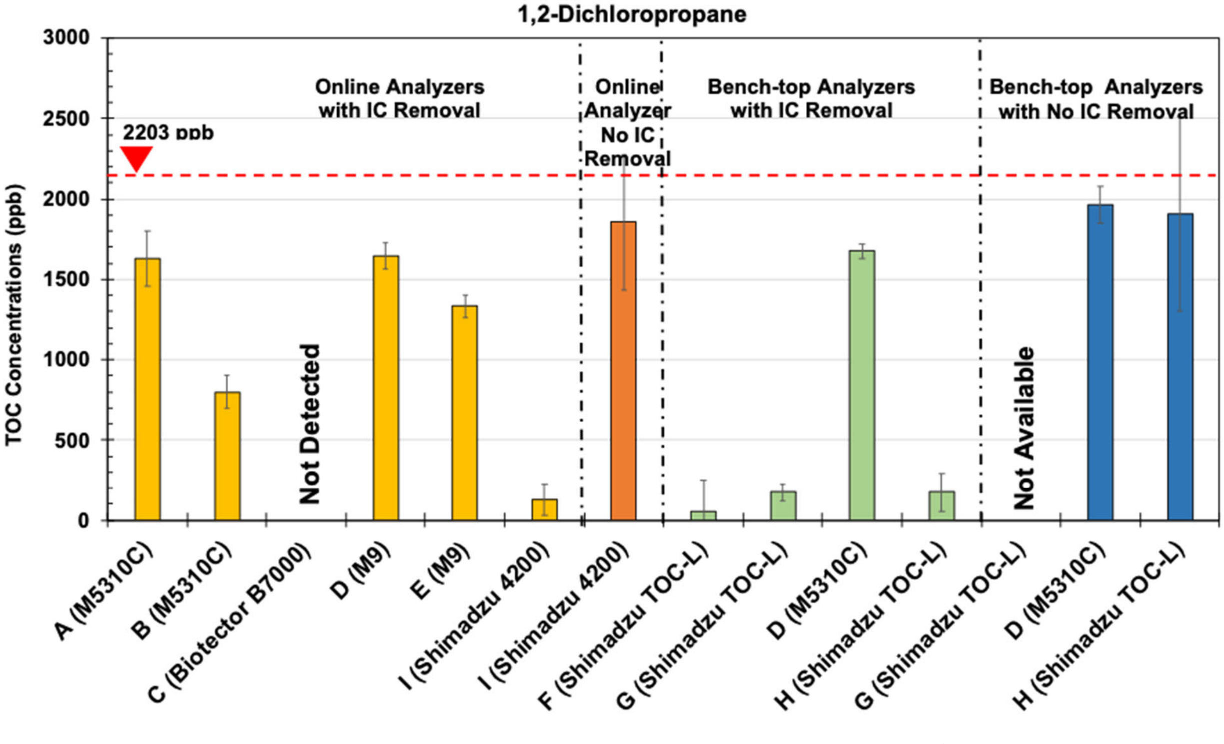

Figure A-14. Measured 1,2-Dichloropropane TOC Concentrations for ROF.
Not Detected: The background concentration was the same or higher than the fortified sample concentration.

Dichloromethane

Recoveries for DCM in ROP from high to low corresponded to the following order for the online analyzers: B (M5310C) (82%) > A (M5310C) (55%) = D & E (M9) (Avg. 56%) > C (Biotector B3500) (3%). The average recoveries for the online and bench-top M5310C and M9 instruments with and without ICR were lower than for 1,2-dichloropropane. DCM has similar volatility to 1,2-dichloropropane, but it is more difficult to oxidize by hydroxyl radicals, which may explain a lower overall recovery for DCM. C (Biotector B3500), again, had poor recovery of DCM. It appears this compound was removed during the ICR process of the Biotector instrument. Poor recovery, Avg. 10%, was also observed for the bench-top Shimadzu instruments with ICR (G and H), indicating removal by the ICR process. The TOC recovery, 55%, for the online instrument A (M5310C) agreed with its bench-top analogs with ICR (56%) (D (M5310C)). However, similar to 1,2-dichloropropane, the TOC recovery for D (M5310C), 87%, was higher with no ICR indicating the similar ICR processes for M5310C and M9 instruments are removing some DCM.

Recoveries for DCM in ROF from high to low corresponded to the following order for the online analyzers: D & E (M9) (Avg. 60%) > A & B (M5310C) (Avg. 52%) > I (Shimadzu 4200) (0%) = C (Biotector B7000) (0%). Like ROP, the average recoveries for the online and bench-top M5310C and M9 instruments with and without ICR were lower than for 1,2-dichloropropane. C (Biotector B7000) and I (Shimadzu 4200) instruments again had very poor recovery of DCM, such as in ROP. However higher recovery, 71%, was observed for the online instrument I (Shimadzu 4200) with ICR off, suggesting the ICR process purged DCM for instrument I (Shimadzu 4200). It appears this compound was also removed during the ICR process of the Biotector instrument. The TOC recovery data, 54%, for the online instrument A (M5310C) agreed with its bench-top analogs with ICR (57%) (D (M5310C)). Similar to ROP, the TOC recovery for D (M5310C), 74%, was higher with no ICR indicating the similar ICR processes for M5310C and M9 instruments are removing some DCM.

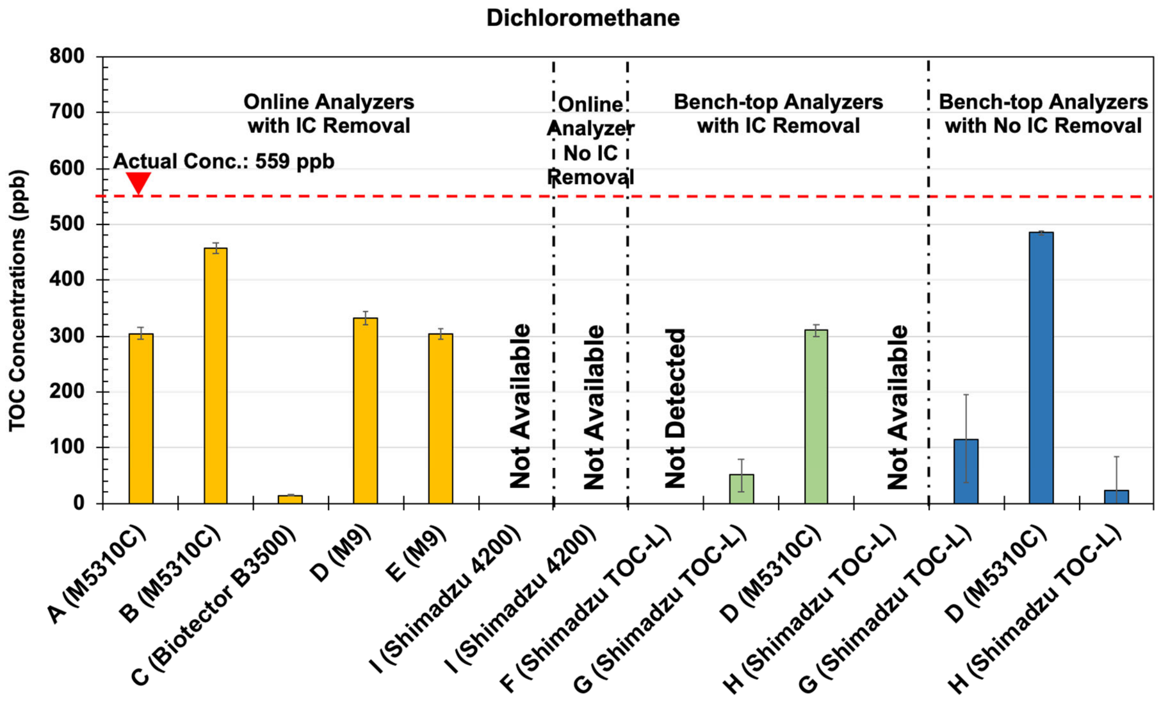

Figure A-15. Measured DCM TOC Concentrations for ROP.

Not Detected: The background concentration was the same or higher than the fortified sample concentration.

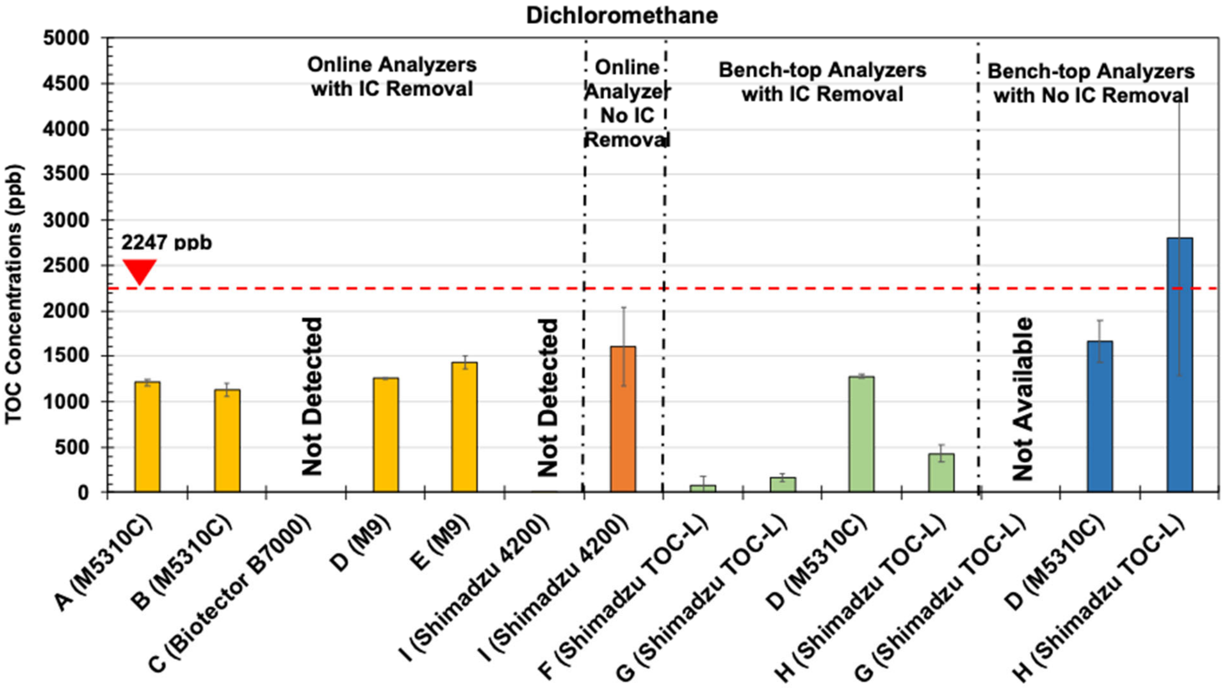

Figure A-16. Measured DCM TOC Concentrations for ROF.

Not Detected: The background concentration was the same or higher than the fortified sample concentration.

Carbon Disulfide

Poor recoveries for carbon disulfide were observed for all the online analyzers for both ROP and ROF with an overall average of 7%. It appears this compound was removed during the ICR process of the Sievers M5310C and M9, Biotector B3500/B7000, and Shimadzu 4200 and TOC-L instruments. This was supported by the higher TOC performance recoveries observed for A (M5310C), D (M5310C), I (Shimadzu 4200; ROF only), and H (Shimadzu TOC-L; ROF only) instruments with no ICR. However, these TOC performance recoveries without ICR were also low (17-57%) relative to the other compounds. As the most volatile among the target VOCs it may have volatilized from vials or reservoirs within the instruments even without sparging.

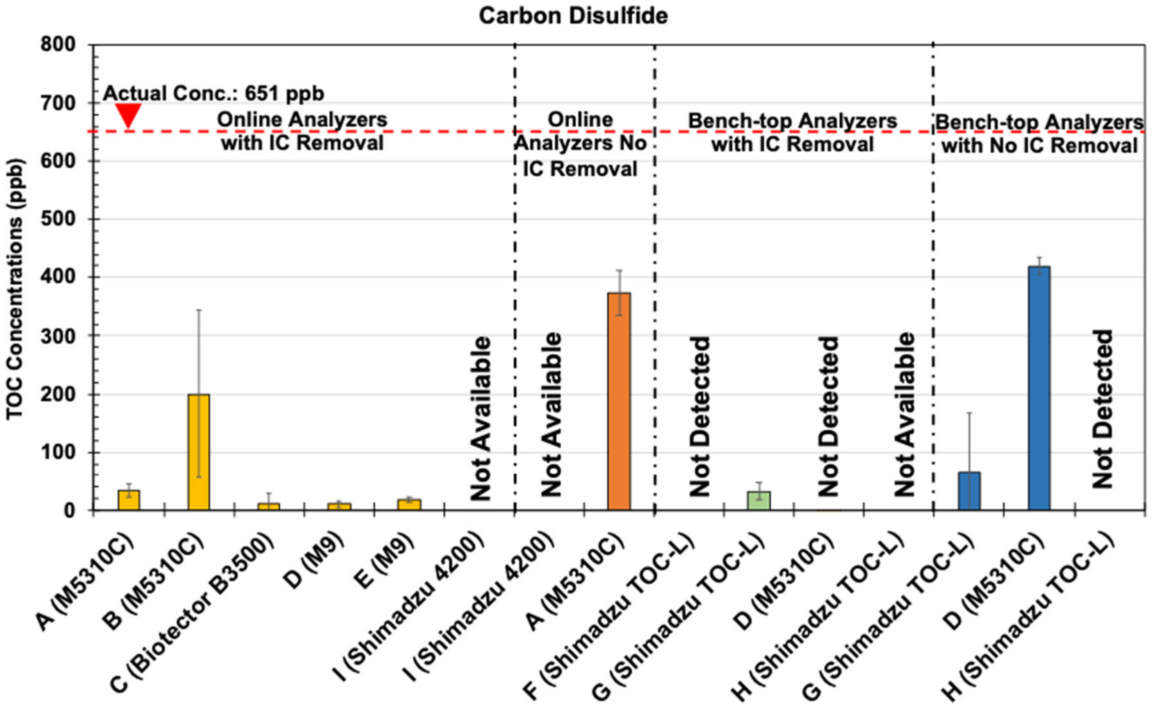

Figure A-17. Measured Carbon Disulfide TOC Concentrations for ROP.

Not Detected: The background concentration was the same or higher than the fortified sample concentration.

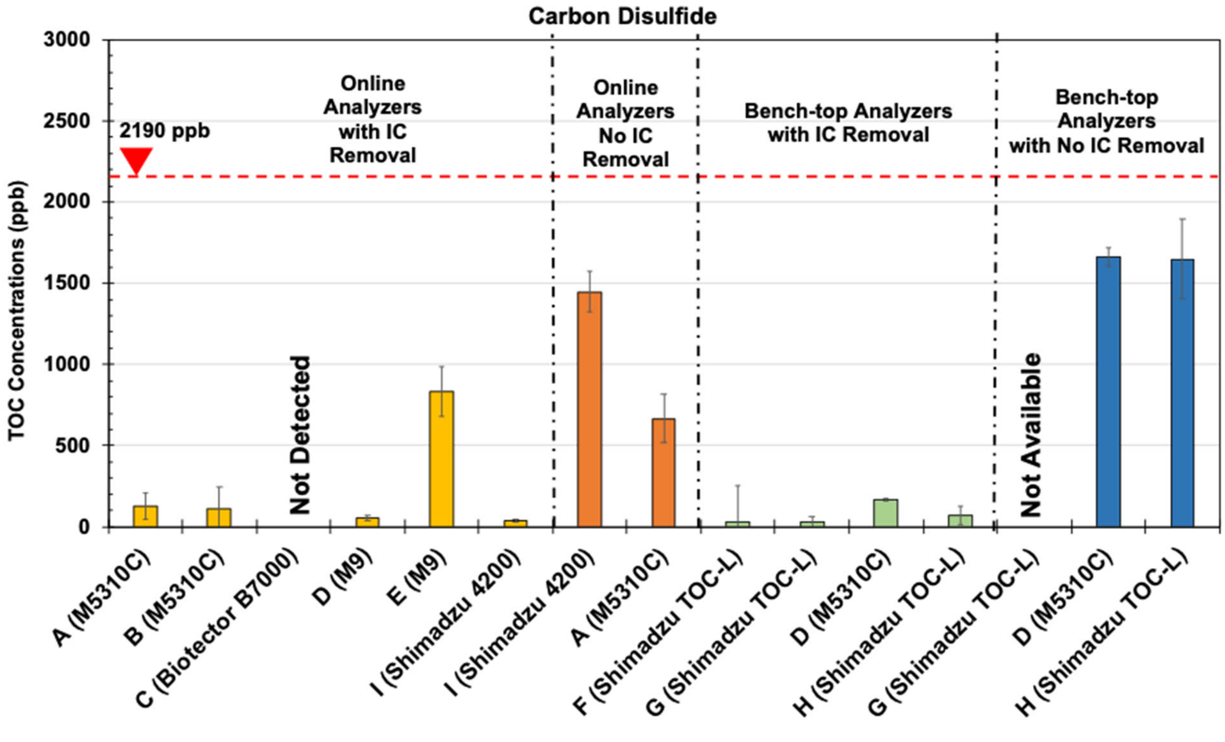

Figure A-18. Measured Carbon Disulfide TOC Concentrations for ROF.

Not Detected: The background concentration was the same or higher than the fortified sample concentration.

VOC Mixture

Considering ROP and ROF, the TOC performance recoveries for the VOC mixture from high to low followed the following order for the online analyzers: D (M9) = A (M5310C) > I (Shimadzu 4200) > C (Biotector B3500/B7000) (Table A-14). However, most of the TOC performance recoveries were outside of ± 15%. Interestingly for ROP, unlike the individual spiking results for acetone, MIBK, and 1,2-dichloropropane results, B (M5310C) (74%) and E (M9) (65%) performed similar to their analogs, A (M5310C) (71%) and D (M9) (72%), respectively. However, for ROF, as observed before, B (M5310C) (28%) and E (M9) (44%) did not perform as well as their analogs, A (M5310C) (70%) and D (M9) (66%), respectively. For both ROP and ROF the TOC performance recoveries for the online instrument A (M5310C) (~70%) with ICR-On agreed with its bench-top analog with ICR-On, D (M5310C) (~66%), though higher recoveries were observed for online, A (M5310C) (~78%), and bench-top, D (M5310C) (~83%), instruments with ICR-Off. For ROF the TOC data for the online instrument I (Shimadzu 4200) (37%) agreed with its bench-top analogs with ICR, G-H (Shimadzu TOC-L) (~42%), though higher recovery was observed with no ICR; bench-top analyzer, H (Shimadzu TOC-L) (79%), and online analyzer, I (Shimadzu 4200) (85%). Higher overall recoveries were observed for the RO permeate than Feed with online analyzers.

Similar to acetone and MIBK results, the bench-top Shimadzu TOC-L with ICR-On (participants F, G, and H) varied in calculated recovery values for ROP (21-40%) and ROF (27-43%). This could be due to differing conditions for purging (i.e., rate, time) that impacted the VOC removal. Also, for ROP and ROF, the bench-top Shimadzu TOC-L with ICR-Off (participants G and H) had variable TOC performance recoveries and low precision (outside ± 6% RSD). This is likely due to the magnification of RSD in the difference when subtracting variables.

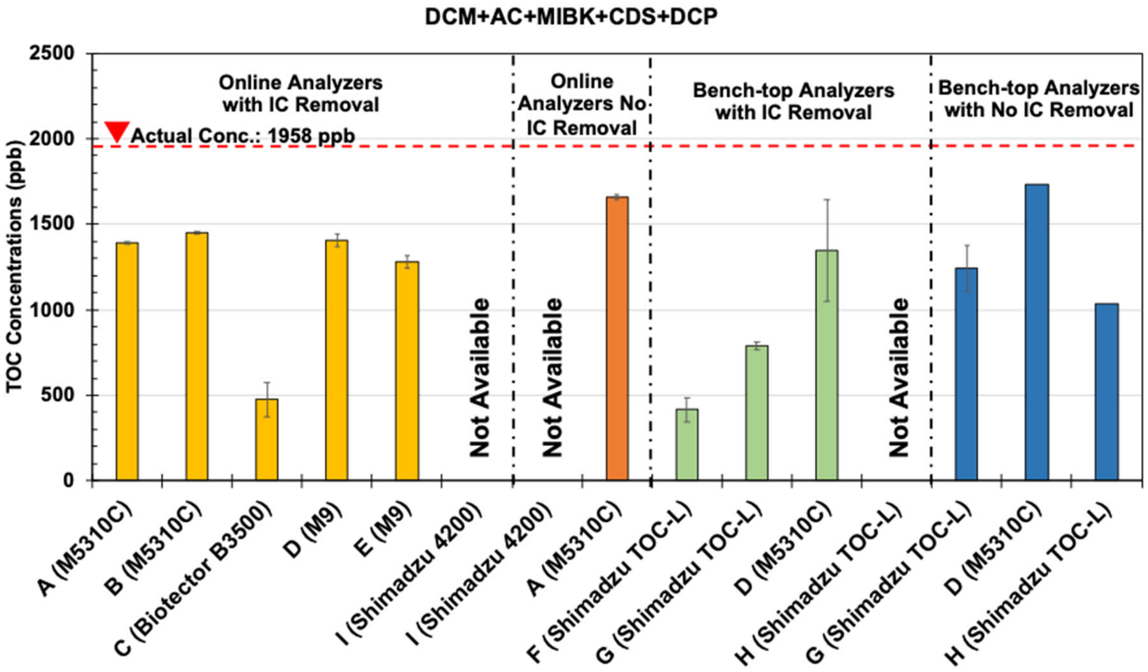

Figure A-19. Measured VOC Mixture TOC Concentrations for ROP.

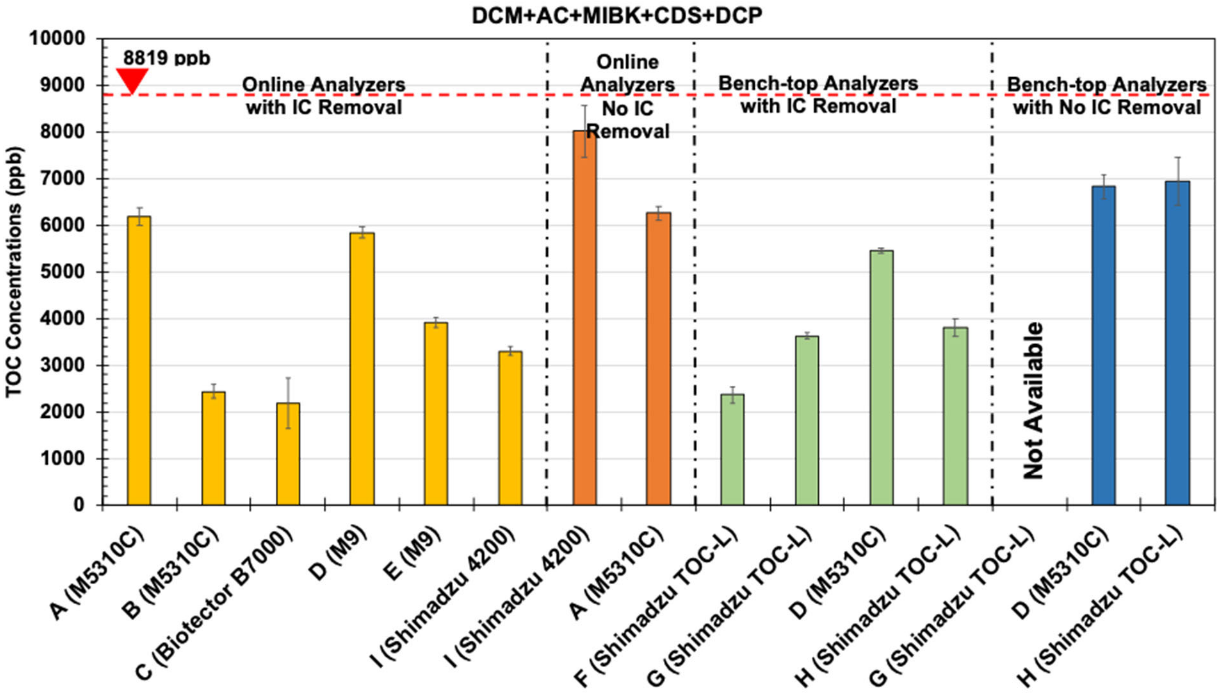

Figure A-20. Measured VOC Mixture TOC Concentrations for ROF.

A.3.3.3 Impact of Volatility and Oxidation on TOC Performance Recovery

Log H_{yc} versus TOC recoveries are reported ROP and ROF in Figures A-21 and A-22. The figures indicate that TOC recoveries for target VOCs decreased with increasing H_{yc}. Among the tested analyzers, the bench-top D (M5310C) analyzer (ICR-Off) performed the best under varying H_{yc} values. When comparing the recoveries for the bench-top M5310 ICR-On and -Off, the results indicate the IC removal lowered the TOC recoveries for M5310C with ICR-On. The recovery performance significantly drops off above H_{yc} of ~0.2 across the PUO instruments. Correlations between TOC recoveries for the PUO and TSAO instruments and the compound's hydroxyl radical rate constants were not observed suggesting lower recoveries were less influenced by incomplete oxidation.

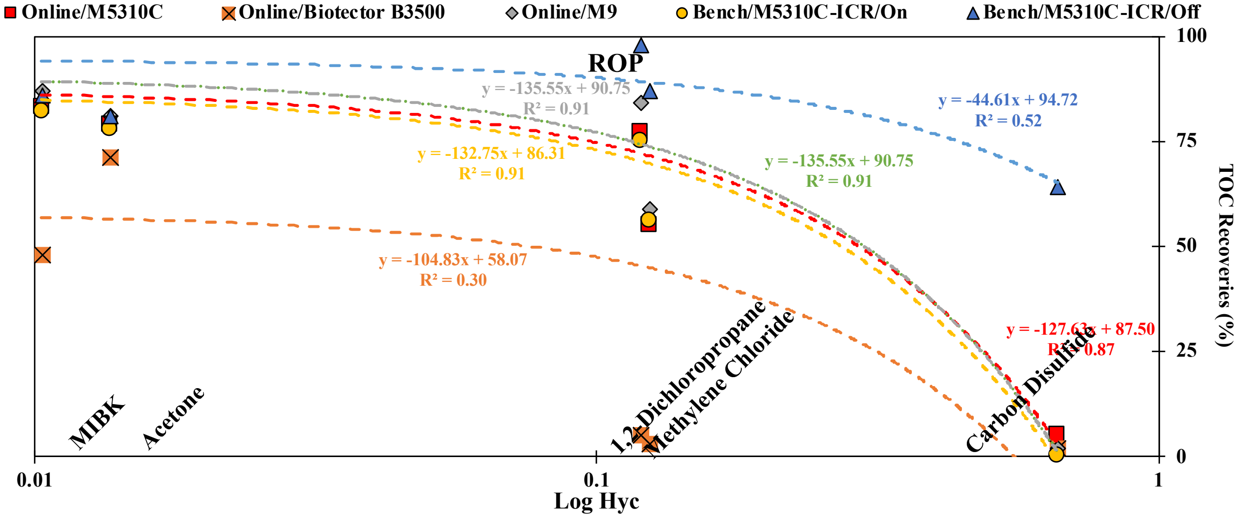

Figure A-21. Plot of % VOC Recoveries vs. H_{yc} for ROP.

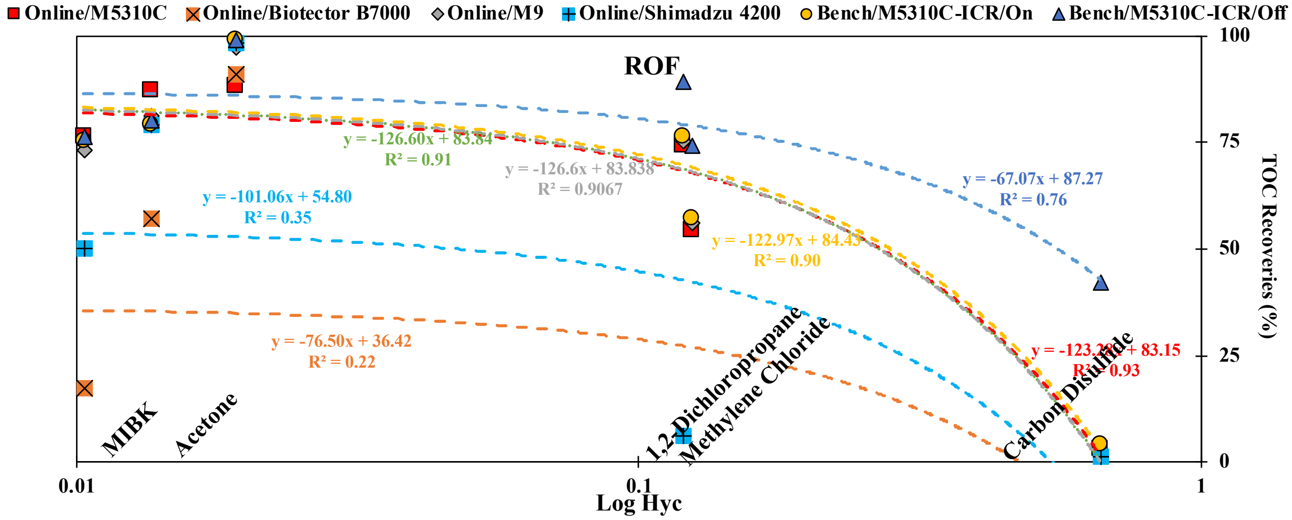

Figure A-22. Plot of % VOC Recoveries vs. H_{yc} for ROF.

A.4 Conclusions

Overall, the VOC holding recovery results for ROP and ROF indicated minimal loss of the VOCs during the preparation of samples and transport to participating sites. Based on Standard Methods 5310 an acceptable TOC performance recovery for fortified samples is not less than 85% and no more than 115%. Only two instruments satisfied this recovery criteria for ROP: online D (M9) instrument for MIBK and 1,2-dichloropropane and the bench-top D (M5310C) with ICR-Off for MIBK, 1,2-dichloropropane, and DCM.

Since most of the TOC performance recoveries were outside of the Standard Methods acceptable recovery range, which may not be applicable for VOCs, and for the purpose of comparing instruments, a ± 20% range for TOC recovery was evaluated. The TOC performance recoveries for the online A (M5310C) and D (M9) instruments were within ± 20% for acetone, MIBK, and 1,2-dichloropropane for ROP (RSD < 5%), however they were only within ± 20% for acetone for ROF (RSD < 3%). The online M5310C and the M9 instruments demonstrated acceptable performance verified by the Suitability System Test for both ROP and ROF waters. However, these same instruments were less accurate for DCM (55-59%) and carbon disulfide (2-5%) for ROP, where these online PUO processes with ICR likely partially (DCM) or fully (carbon disulfide) removed the VOC compounds via the ICR process. This was in agreement with the bench-top D (M5310C) instrument with ICR for ROP; 56% for DCM and 0% for carbon disulfide. VOC removal via vacuum degassing was supported indirectly by the D (M5310C) instrument operated with ICR off, which had a higher TOC performance recovery of 87±1% and 64±2% for DCM and carbon disulfide, respectively, in ROP. However, the carbon disulfide recoveries with the A (M5310C) and D (M5310C) with ICR off were still less than 80% and even 70% for ROP. Even though A (M5310C) and D (M5310C) showed lower performance recoveries with ICR off, it demonstrated acceptable performance verified by the Suitability System Test. Therefore, operating a PUO online with ICR off could result in a more accurate and precise measurements and be a consideration, if more volatile compounds (i.e., DCM and carbon disulfide) are expected to be present in the sample flow. For example, higher recovery was observed for the online A (M5310C) instrument with ICR off for the individually spiked sample with carbon disulfide and the mixture sample (Figures A-17- A-20), though this should also be verified for less volatile VOCs than carbon disulfide for online PUO systems. Interestingly, online PUO instruments, B (5310C) and E (M9), did not have acceptable recoveries for any of the target VOCs, though they demonstrated acceptable performance verified by the Suitability

System Test. Further investigation is warranted to more clearly understand why some online PUO instruments perform better than others.

Similar to the online A (M5310C) and D (M9) instruments, the online Shimadzu 4200 at site I only had a performance recovery within ±20% for acetone in ROF (only evaluated for ROF) though the instrument satisfied the acceptable criteria verified by the Suitability System Test. However, when the I (Shimadzu 4200) instrument was operated with ICR off, the TOC performance recoveries were consistently higher, some of which were within ±20%: acetone (88%), MIBK (87%), 1,2-dichloropropane (84%), DCM (71%), and carbon disulfide (35%). Note, operating the online Shimadzu 4200 with ICR off satisfied the acceptable performance criteria verified by the Suitability System Test. Therefore, operating the online Shimadzu 4200 with ICR off, particularly with sample waters with higher TOC like ROF, could be considered if the detection of VOCs is of interest.

It is not recommended to substitute an online monitoring TOC instrument with ICR with an instrument with ICR off. The primary purpose of the online TOC instrument is to continuously monitor for the TOC removal performance across a RO membrane. An instrument with ICR off (i.e., PUO instruments) will have difficulty measuring accurate TOC in ROP or ROF associated with the issue of subtracting a large IC concentration from a large TC concentration to get a relatively small TOC concentration. Because of this, an instrument with ICR off will also have challenges in quantifying a baseline threshold that would be needed to identify an event peak. It might be possible to operate two instruments in tandem, one with ICR and the other with ICR off, but this would need to be verified. The instrument with ICR would evaluate i) TOC removal across the RO, ii) establish a baseline for a potential event peak and iii) capture event peaks from non-purgeable compounds. The instrument with ICR off could capture peaks, specifically those from volatile compounds, though further research is warranted to understand the accuracy and precision of online instruments with ICR off for varying peak levels. Note, additional online monitoring would require additional operational resources that needs to be considered, thus further research is needed to evaluate if there is an absolute need to monitor for VOCs associated with wastewater treatment.

The online Biotector TSAO instruments did not have acceptable TOC performance recoveries for any of the VOC compounds in both ROP and ROF. The Biotector B3500 (ROP) did not demonstrate acceptable performance verified by the Suitability System Test, whereas the Biotector B7000 (ROF) did. In summary the ranking of the types of online TOC instruments is the following: PUO (M5310C, M9) > HTC (Shimadzu 4200) > and TSAO (Biotector B3500).

There appears to be a relationship between the TOC performance recovery of a VOC and H_{yc} of the VOC (Figures A-21 - A-22). VOC compounds with a $H_{yc} < 0.014$ (i.e., acetone and MIBK) had better recovery for the online A (M5310C) and D (M9) instruments for ROP. However, the opposite was true for compounds with a higher H_{yc} (>0.67), like carbon disulfide. Better recovery for 1,2-dichloropropane, H_{yc} 0.12, was observed by the online A (M5310C) and D (M9) instruments for ROP than for DCM, even though DCM has a similar H_{yc} of 0.124. The recovery performance significantly dropped off above H_{yc} of ~0.2 across the PUO instruments. However, the exact threshold between H_{yc} of > 0.014 and < 0.67 for acceptable level of performance to allow detection of VOC is unclear and could be better defined by further research. In addition, further research is warranted to understand if other factors are important for ICR for PUO instruments and the accuracy of the measured (such as accounting for actual water temperature) or estimated H_{yc} constants (determining H_{yc} values experimentally for compounds that have limited or no literature data on measurement of Henry's law constants). Since Henry's law volatility constant is an important parameter for application of TOC instruments to detect VOCs, the System Suitability Test should include compounds that are both challenging to oxidize and volatile.

Aerobic aeration is practiced in wastewater treatment before an advanced potable reuse train. Therefore, some VOCs are likely stripped from the aqueous phase during aeration. Understanding which VOCs are typically air-stripped and relative degree of their removal, would be important in regard to knowing which types of VOCs would be of higher concern for relying on their detection in downstream treatment steps in a potable reuse train and which ones are of lesser concern. For example, if highly volatile organic compounds (such as carbon disulfide) are consistently removed via pretreatment aeration, then there would be less of a dependence on the online TOC instruments to detect those types of compounds. However, it is possible that an industrial spill could release such a large quantity of a VOC that it could be still detectable after wastewater treatment aeration and RO. In such cases, having an on-line TOC meter provides at least some level of detection of such events and allows the facility to respond to further ascertain the extent of the event. Also, VOCs could be created within wastewater treatment and reuse treatment and then pass through RO (e.g., biological metabolites, DBPs, oxidation products). For example, the observed acetone peak at Orange County Water District's Groundwater Replenishment System in California (Marron et al. 2019), was attributed to Isopropyl alcohol that was oxidized to acetone within the wastewater treatment. Subsequently, a TOC peak was detected in ROF and ROP and identified to be from acetone. However, more research is warranted to understand to what extent different types of VOCs are removed during secondary treatment aeration.

Interestingly, the bench-top Shimadzu TOC-L analyzers with ICR had variable TOC performance recovery values for some of the VOCs and this could be due to differing conditions for purging (i.e., rate, time) that directly impacted the degree of VOC removal. A better understanding of these purging conditions is warranted to optimize the recovery of VOC compounds by bench-top Shimadzu TOC-L analyzers. Also, operating the bench-top Shimadzu TOC-L analyzers with ICR off appears to be not effective in capturing the individually spiked VOC recoveries for ROP.

References

Ahmed, M.B, J.L. Zhou, W. Guo, N.S. Thomaidis, and J. Zu. 2017. “Progress in the Biological and Chemical Treatment Technologies for Emerging Contaminant Removal from Wastewater: A Critical Review.” *Journal of Hazardous Materials*, 323: 274-298.

Alotaibi, M.D., B.M. Patterson, A.J. McKinley, A.Y. Reeder, and A.J. Furness. 2015. “Benzotriazole and 5-methylbenzotriazole in Recycled Water, Surface Water and Dishwashing Detergents from Perth, Western Australia: Analytical Method Development and Application.” *Environmental Science: Processes & Impacts*, 17 (2): 448-457.

Bahnmüller, S., C.H. Loi, K.L. Linge, U.V. Gunten, and S. Canonica. 2015. “Degradation Rates of Benzotriazoles and Benzothiazoles Under UV-C Irradiation and the Advanced Oxidation Process UV/H2O2.” *Water Research*, 74 (1): 143-154.

Bellona, C., J.E. Drewes, P. Xu, and G. Amy. 2004. “Factors Affecting the Rejection of Organic Solutes During NF/RO treatment—a Literature Review.” *Water Research,* 38: 2795-2809.

Bernados, B. 2018. “Reverse Osmosis for Direct Potable Reuse in California.” *J AWWA,* 110. doi:10.1017/CBO9781107415324.004.

Breitner, L.N., K.J. Howe, and D. Minakata. 2018. “Boron Can Be Used to Predict Trace Organic Rejection through Reverse Osmosis Membranes for Potable Reuse.” *Environ. Sci. Technol.* doi:10.1021/acs.est.8b03390.

Breitner, L.N., K.J. Howe, and D. Minakata. 2019. “Effect of Functional Chemistry on the Rejection of Low-Molecular Weight Neutral Organics through Reverse Osmosis Membranes for Potable Reuse.” *Environ. Sci. Technol.* doi:10.1021/acs.est.9b03856.

Burrows, L.J., A.J. Stokes, J.R. West, C.F. Forster, and A.D. Martin. 1999. “Evaluation of Different Analytical Methods for Tracer Studies in Aeration Lanes of Activated Sludge Plants.” *Water Research,* 33 (2): 367-374.

Buxton, G.V., C.L. Greenstock, W.P. Helman, A.B. Ross, and W. Tsang. 1988. “Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals (•OH/•O-) in Aqueous Solution." *Journal of Physical and Chemical Reference Data,* 17: 513-886.

California Water Boards. 2020. “Drinking Water Notification Levels.” Accessed 11.17.20. https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/NotificationLevels.html.

Chen, F., D.L. Freedman, R.W. Falta, and L.C. Murdoch. 2012. “Henry’s Law Constants of Chlorinated Solvents at Elevated Temperatures.” *Chemosphere*, 86 (2012) 156–165.

City of San Diego. 2017. “2017 Pretreatment Program Annual Report for the Point Loma POTW.” Accessed July 15, 2019. https://www.sandiego.gov/public-utilities/sustainability/wastewater-plant-monitoring.

City of San Diego. 2019. *Final Draft Title 22 Engineering Report - North City Pure Water Facility*. https://www.sandiego.gov/sites/default/files/north_city_pure_water_project_final_draft_title_22_engineering_report.pdf.

Crittenden, J.C., R.R. Trussell, D.W. Hand, K.J. Howe, and G. Tchobanoglous. 2012. *Water Treatment Principles and Design.* 3rd Edition. Hoboken, New Jersey: John Wiley & Sons, Inc.

Dadakis, J., and B. Dunivin. 2013. February 2013 Acetone/TOC Occurrence. Panel, G.R.S.N.I.A. (ed). NWRI.

Doederer, K., M.J. Farré, M. Pidou, H.S. Weinberg, and W. Gernjak. 2014. "Rejection of Disinfection By-Products by RO and NF Membranes: Influence of Solute Properties and Operational Parameter." *Journal of Membrane Science*, 467: 195-205.

Drewes, J.E., P. Xu, C. Bellona, M. Oedekoven, D. Macalady, G. Amy, and T.U. Kim. 2006. *Rejection of Wastewater-Derived Micropollutants in High-Pressure Membrane Applications Leading to Indirect Potable Reuse*. Alexandria, Virginia: WateReuse Foundation.

Drewes, J.E., D. Sedlak, S. Snyder, and E. Dickenson. 2008. *Development of Indicators and Surrogates for Chemical Contaminant Removal during Wastewater Treatment and Reclamation*. Project No: WRF-03-014. Alexandria, Virginia: WateReuse Foundation.

Drewes, J.E., E. Dickenson, and S. Snyder. 2009. *Contributions of Household Chemicals to Sewage and their Relevance to Municipal Wastewater Systems and the Environment*. Project No: 03-CTS-21UR. Water Environment Research Foundation.

Fujioka, T, S.J. Khan, Y. Poussade, J.E. Drewes, and L.D. Nghiem. 2012. "N-nitrosamine Removal by Reverse Osmosis for Indirect Potable Water Reuse – A Critical Review Based on Observations from Laboratory-, Pilot- and Full-Scale Studies." *Separation and Purification Technologies,* 98: 503-515.

Fujioka, T., H. Kodamatani, L.D. Nghiem, and T. Shintani. 2019. "Transport of N-nitrosamines Through a Reverse Osmosis Membrane: Role of Molecular Size and Nitrogen Atoms." *Environmental Science & Technology Letters*, 6 (1): 44-48.

Galloway, L., F. Dolislager, D. Steward, K. Noto, K. Manning, A. Armstrong, and C.E. Samuels. 2020. "The Risk Assessment Information System." Univ. Tennessee. Accessed 8.3.20. https://rais.ornl.gov/index.html.

Gerhold, R., and G. Malaney. 1966. "Structural Determinants in the Oxidation of Aliphatic Compounds by Activated Sludge." *Journal of Water Pollution Control Federation*, 38(4): 562-579.

Gerrity, D., S. Gamage, D. Jones, G.V. Korshin, Y. Lee, A. Pisarenko, R.A. Trenholm, U.V. Gunten, E.C. Wert, and S.A. Snyder. 2012. "Development of Surrogate Correlation Models to Predict Trace Organic Contaminant Oxidation and Microbial Inactivation during Ozonation." *Water Research,* 46: 6257-6272.

Gonzalez, R.K., J. Dadakis, and M. Patel. 2015. "Application of Control Chart Theory for Critical Control Point Monitoring," CA WateReuse Annual Conference. Los Angeles, CA. WaterReuse Foundation

Government of Singapore. 1999. Sewerage and Drainage (Trade Effluent). Chapter 294, Sections 72 and 74. Version in Force from 10/23/2016.

Hoaglin, D.C., B. Iglewicz, and J.W. Tukey. 1986. "Performance of Some Resistant Rules for Outlier Labelling." *Journal of American Statistical Association,* 81: 991-999.

Howe, K. 2019. *Predicting Reverse Osmosis Removal of Unique Organics*. Project Reuse-14-19/4769. The Water Research Foundation.

Hubner, U., U.V. Gunten, and M. Jekel. 2015. “Evaluation of the Persistence of Transformation Products from Ozonation of Trace Organic Compounds- A Critical Review.” *Water Research,* 68: 150-170.

Kempisty D.M., R.S. Summers, G. Abulikemu, N.V. Deshpande, J.A. Rebholz, K. Roberts, and J.G. Pressman. 2019. “Granular Activated Carbon Adsorption of Carcinogenic Volatile Organic Compounds at Low Influent Concentrations.” *AWWA Water Science,* 1 (2): e1128.

Kibler, R., B. Mohrhardt, M. Zhang, L. Breitner, and K.J. Howe. 2020. “Group Contribution Method to Predict the Mass Transfer Coefficients of Organics through Various RO Membranes.” *Environ. Sci. Technol.*, 54: 5167–5177. https://doi.org/10.1021/acs.est.9b06170.

Kiso, Y., K. Muroshige, T. Oguchi, M. Hirose, T. Ohara, and T. Shintani. 2011. “Pore Radius Estimation Based on Organic Solute Molecular Shape and Effects of Pressure on Pore Radius for a Reverse Osmosis Membrane.” *Journal of Membrane Science,* 369: 290-298.

Knappe, D. 2017. *Evaluation of Henry’s Law Constants and Freundlich Adsorption Constants for VOCs*. Project 4462. Water Research Foundation.

Laurent, J., R.W. Samstag, J.M. Ducoste, A. Griborio, I. Nopens, D.J. Bastone, J.D. Wicks, S. Saunders, and O. Potier. 2014. “A Protocol for the Use of Computational Fluid Dynamics as a Supportive Tool for Wastewater Treatment Plant Modelling.” *Water Science & Technology,* 70 (10): 1575-1584.

Leverenz, H.L., and G. Tchobanoglous. 2011. “Direct Potable Reuse: A Future Imperative.” *Journal of Water Reuse and Desalination*, 1(1), 2-10.

Linge, K.L., P. Blair, F. Busetti, C. Rodriguez, and A. Heitz. 2012. “Chemicals in Reverse Osmosis-Treated Wastewater: Occurrence, Health Risk, and Contribution to Residual Dissolved Organic Carbon.” *J. Water Supply Res. Technol. – AQUA*, 61: 494–505. doi:10.2166/aqua.2012.047.

Marron, E.L., W.A. Mitch, U. Von Gunten, and D.L. Sedlak. 2019. “A Tale of Two Treatments: The Multiple Barrier Approach to Removing Chemical Contaminants During Potable Water Reuse.” *Acc. Chem. Res.*, 52: 615–622. doi:10.1021/acs.accounts.8b00612.

Marron, E.L., C. Prasse, J. Van Buren, and D.L. Sedlak. 2020. “Formation and Fate of Carbonyls in Potable Water Reuse Systems.” *Environ. Sci. Technol.* doi:10.1021/acs.est.0c02793.

Mestankova, H., A.M. Parker, N. Bramaz, S. Canonica, K. Schirmer, U. von Guten, and K.G. Linden. 2016. “Transformation of Contaminant Candidate List (CCL3) Compounds During Ozonation and Advanced Oxidation Processes in Drinking Water: Assessment of Biological Effects.” *Water Research,* 93: 110-120.

National Library of Medicine. 2020. PubChem. NIH. Accessed 6.17.20. pubchem.ncbi.nlm.nih.gov.

NRC (National Research Council). 2012. *Water Reuse: Potential for Expanding the Nation’s Water Supply Through Reuse of Municipal Wastewater*. Washington, DC: National Academies Press.

OC San (Orange County Sanitation District). 2015. “2014-15. Pretreatment Program Annual Report.” Accessed July 15, 2019. https://www.ocsd.com/about-us/transparency/annual-reports/

OCWD (Orange County Water District). 2013a. ”GWRS Annual Reports.” Accessed June 5, 2019. https://www.ocwd.com/gwrs/annual-reports/.

OCWD (Orange County Water District). 2013b. Required Reporting of Temporary TOC Concentration Excursion in BWRS-FPW. Letter to California Regional Water Quality Control Board (RWQCB), April 19, 2013.

OCWD (Orange County Water District). 2015. *GWRS Operation Optimization Plan*. Prepared by DDB Engineering, Inc.

Olivieri, A., J. Crook, M. Anderson, R. Bull, J. Drewes, C. Haas, W. Jukubowski, P. McCarty, K. Nelson, J. Rose, D. Sedlak, and T. Wade. 2016. *Expert Panel Final Report: Evaluation of the Feasibility of Developing Uniform Water Recycling Criteria for Direct Potable Reuse, Report State Water Resources Control Board Division of Drinking Water.* Sacramento, California.

Patel, M. 2014. “OCWD's Groundwater Replenishment System Uses Critical Control Points to Monitor Project Performance.” *AWWA*, 28 (3): 10-12.

Pecson, B.M., R.S. Trussell, A.N. Pisarenko, and R.R. Trussell. 2015. “Achieving Reliability in Potable Reuse: The Four Rs.” *JAWWA*, 3(107): 48-58.

Plumlee, M., M. Lopez-Mesas, A. Heidlberger, K.P. Ishida, and M. Reinhard. 2008. “N-nitrosodimethylamine (NDMA) Removal by Reverse Osmosis and UV Treatment and Analysis via LC-MS/MS.” *Water Research,* 42: 347-355.

Potier, O., J.-P. Leclerc, and M.-N. Pons. 2005. “Influence of Geometrical and Operational Parameters on the Axial Dispersion in an Aerated Channel Reactor.” *Water Research,* 39: 4454-4462.

Prasse, C., D. Stalter, U. Schulte-Oehlmann, J. Oehlmann, and T.A. Ternes. 2015. “Spoilt for Choice: A Critical Review on the Chemical and Biological Assessment of Current Wastewater Treatment Technologies.” *Water Research,* 87: 237-270.

PUB (Singapore Public Utility Board). 2014. *Innovation in Water Singapore: An R&D publication of Public Utility Board, Singapore’s National Water Agency.* PUB.

Rodriguez, C., K. Linge, P. Blair, F. Busetti, B. Devine, P.V. Buynder, P. Weinstein, and A. Cook. 2012. “Recycled Water: Potential Health Risks from Volatile Organic Compounds and Use of 1,4-Dichlorobenzene as Treatment Performance Indicator.” *Water Research*. 46: 93-106.

Salveson, A. 2018. *Blending Requirements for Water from Direct Potable Reuse Treatment Facilities*. Project 4536. The Water Research Foundation.

Sander, R. 2015. „Compilaton of Henry’s Law Constants (version 4.0) for Water as Solvent.“ *Atmospheric Chemistry and Physics*, 15: 4399-4981.

Schmidt, T.C., M. Schirmer, H. Weiß, and S.B. Haderlein. 2004. „Microbial Degradation of methyl tert-butyl ether and tert-butyl alcohol in the Subsurface.” *Journal of Contaminant Hydrology*, 70(3-4): 173-203.

Snyder, S.A., S. Adham, A.M. Redding, F.S. Cannon, J. DeCarolis, J. Oppenheimer, E.C. Wert, and Y. Yoon. 2007a. “Role of Membranes and Activated Carbon in the Removal of Endocrine Disruptors and Pharmaceuticals.” *Desalination*, 202 (1-3): 156-181.

Snyder, S.A., E.C. Wert, H.D. Lei, P. Westerhoff, and Y. Yoon. 2007b. *Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment Processes*. Project 331. Am. Water Work. Assoc. Res. Found.

Soon, T.Y., T.J. Lee, and K. Tan. 2009. *Clean, Green and Blue - Singapore's Journey Towards Environmental and Water Sustainability*. Singapore: ISEAS.

SM (Standard Methods). 2015. *5310 Total Organic Carbon.* Standard Methods for the Examination of Water and Wastewater, American Public Health Association.

Staudinger, J., and P.V. Roberts. 2001. “A Critical Compilation of Henry's Law Constant Temperature Dependence Relations for Organic Compounds in Dilute Aqueous Solutions.” *Chemosphere*, 44: 561-576.

Swancutt, K., M.K. Dali, S.P. Mezyk, and K.P. Ishida. 2010. “Absolute Kinetics and Reaction Efficiencies of Hydroxyl-Radical-Induced Degradation of Methyl Isothiocyanate (MITC) in Different Quality Waters.” *Chemosphere,* 81: 339-344.

Tackaert, R., A.N. Pisarenko, E.C. Chen, A. Kolakovsky, B.M. Pecson, J.E. Drewes, R.R. Trussell, and R.S. Trussell. 2019. “Demonstrating Process Robustness of Potable Reuse Trains During Challenge Testing with Elevated Levels of Acetone, Formaldehyde, NDMA, and 1,4-Dioxane.” *Journal of Water Supply and Technology-AQUA*, 68 (3): 313-324.

Tchobanoglous, G., J. Cotruvo, J. Crook, E. McDonald, A. Olivieri, A. Salveson, and R.S. Trussell. 2015. *Framework for Direct Potable Reuse*. Alexandria, VA: WateReuse Foundation.

Tukey, J.W. 1977. *Exploratory Data Analysis*. Reading, MA: Addison-Wesley.

USEPA (U.S. Environmental Protection Agency). 2009. *Method 415.3 Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water*. EPA Document: EPA/600/R-09/122.

USEPA (U.S. Environmental Protection Agency). 2011. *Introduction to the National Pretreatment Program*. Cincinnati, OH: U.S. Environmental Protection Agency.

USEPA (U.S. Environmental Protection Agency). 2020a. “CompTox Chemicals Dashboard.” https://comptox.epa.gov/dashboard.

USEPA (U.S. Environmental Protection Agency). 2020b. “National Primary Drinking Water Regulations.” United States Environ. Prot. Agency. Accessed 4.1.20. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.

Verliefde, A.R.D. 2008. Rejection of Organic Micropollutants with High Pressure Membranes (NF/RO). Doctoral thesis, Delft University of Technology. http://resolver.tudelft.nl/uuid:379c9ed2-b4c0-4dc9-acca-e99dfc3469d6.

Weinberg, H.S., W.H. Glaze, S.W. Krasner, and M.J. Sclimenti. 1993. “Formation and Removal of Aldehydes in Plants That Use Ozonation.” *Journal AWWA,* 85 (5): 72-85.

Worthington, E.K., and E.A. Wade. 2007. “Henry’ Law Coefficients of Chloropicrin and Methyl Isothiocyanate.” *Atmospheric Environment*, 41: 5510-5515.

Yang, Y., J.J. Pignatello, J. Ma, and W.A. Mitch. 2016. “Effect of Matrix Components on UV/H2O2 and UV/S2O82- Advanced Oxidation Processes for Trace Organic Degradation in Reverse Osmosis Brines from Municipal Wastewater Reuse Facilities.” *Water Res.*, 89: 192–200. doi:10.1016/j.watres.2015.11.049.

Yangali-Quintanilla, V., A. Verliefde, T.-U. Kim, A. Sadmani, M. Kennedy, and G. Amy. 2009. “Artificial Neural Network Models based on QSAR for Predicting Rejection of Neutral Organic Compounds by Polyamide Nanofiltration and Reverse Osmosis Membranes.” *Journal of Membrane Science,* 342 (1-2): 251-262.

Yalkowsky, S.H., and R.M. Dannenfelser. 1992. *The Aquasol Database of Aqueous Solubility*. Fifth Ed, Tucson, AZ: University of Arizona, College of Pharmacy.

Yoon, Y., and R.M. Lueptow. 2005. “Removal of Organic Contaminants by RO and NF Membranes.” *Journal of Membrane Science*, 261 (1): 76-86.

Zeng, T., M.J. Plewa, and W.A. Mitch. 2016. “N-nitrosamines and Halogenated Disinfection Byproducts in the U.S. Full Advanced Treatment Trains for Potable Reuse.” *Water Research*, 102: 176-186.

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