REAL-TIME DETECTION OF VOLATILE ORGANIC COMPOUNDS IN RO-BASED POTABLE REUSE

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Online Organic Carbon Monitoring for Reverse Osmosis (RO)

- Can measure online “TOC” in RO permeate water: 100-200 µg/L.
- Online “TOC” is used as a surrogate for pathogen removal for RO.
- Online “TOC” is used for compliance in meeting a final product water TOC goal.
- **Online “TOC” can be used to detect episodic chemical peaks.**

Detection of Chemical Peaks in Potable Reuse

Low molecular weight chemicals are important to potable reuse projects

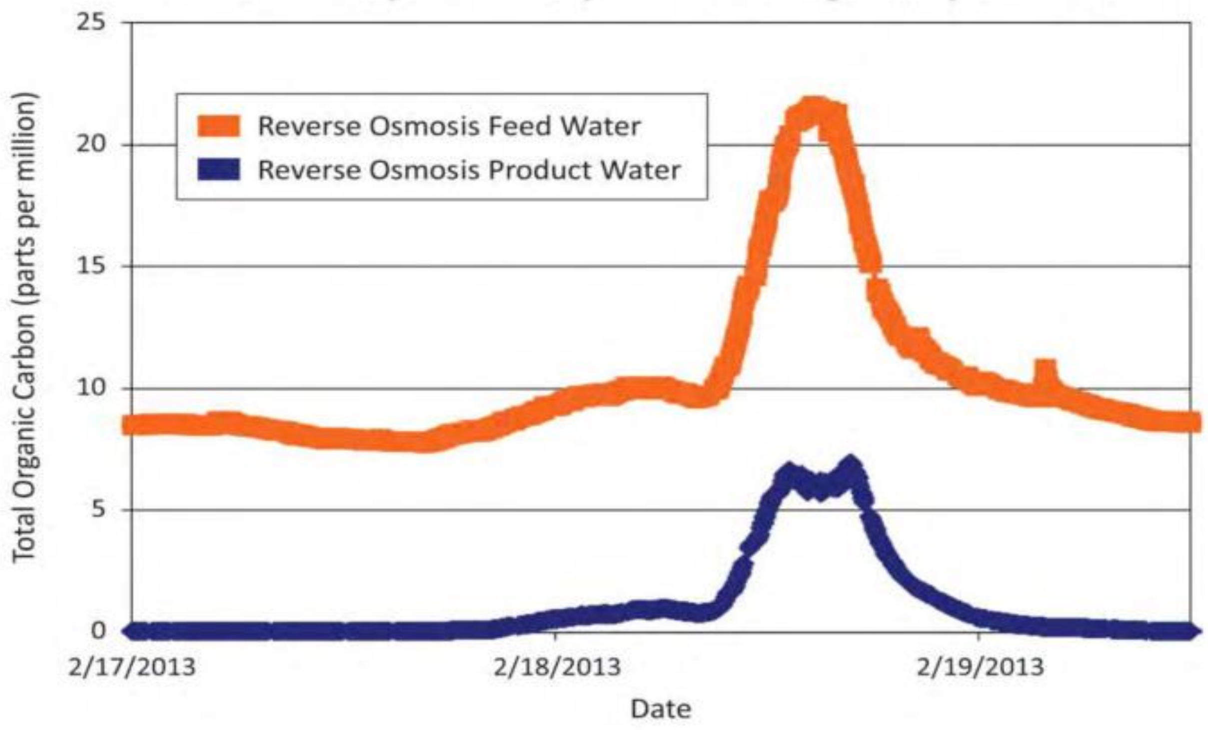
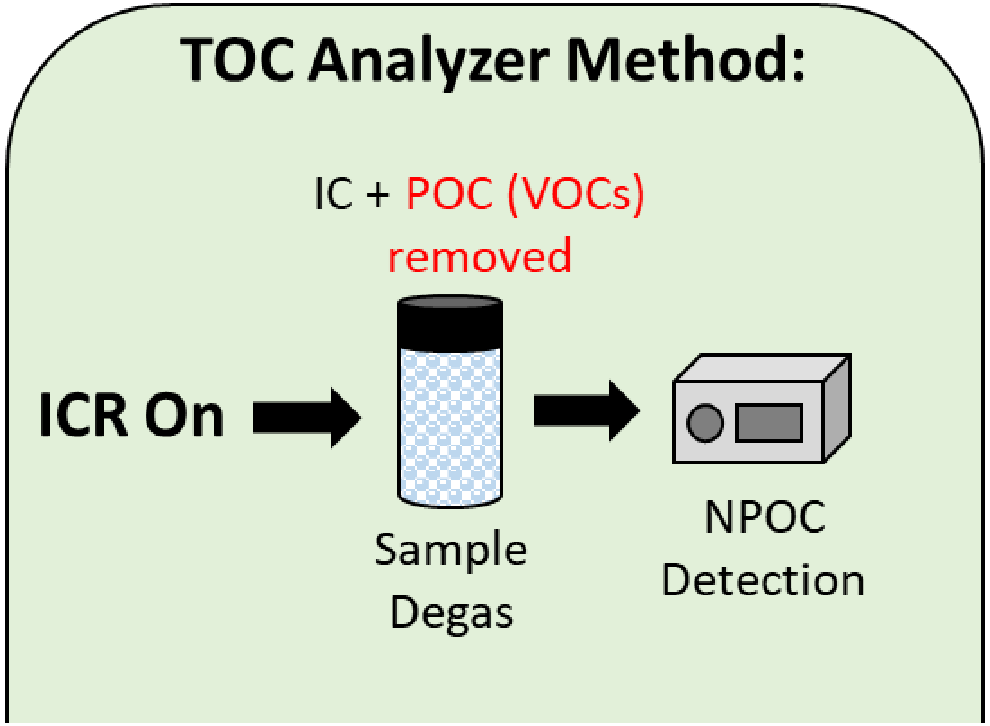


Figure 1-2. Chemical Peak at Orange County Water District's Full-Scale Potable Reuse Facility.
Source: Dadakis and Dunivin 2013.

Debroux, J., Plumlee, M., Trussell, S. **2021,** Defining Potential Chemical Peaks and Management Options, WRF #4991.

VOCs May Not be Detected by Online NPOC Analyzers



TOC – Organic Carbon
IC – Inorganic Carbon
ICR – Inorganic Carbon Removal
POC – Purgeable Organic Carbon Removal
VOCs – Volatile Organic Compounds
NPOC – Nonpurgeable Organic Carbon

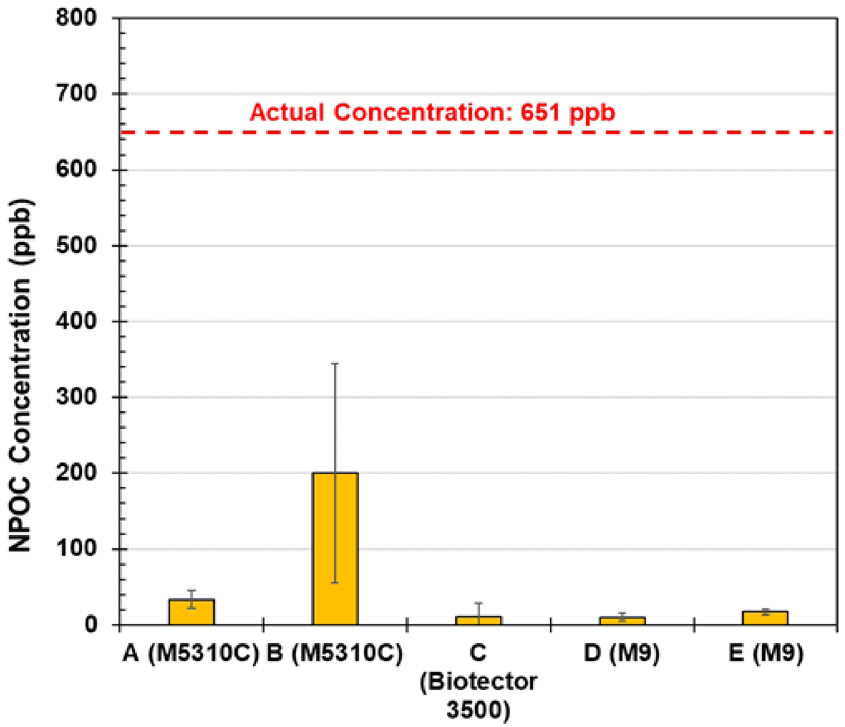


Figure 2. Carbon disulfide concentrations (as NPOC) for reverse osmosis permeate spiked with carbon disulfide at 651 ppb as carbon. Online TOC instruments were operated with IC removal.

Debroux, J., Plumlee, M., Trussell, S. **2021,** Defining Potential Chemical Peaks and Management Options, WRF #4991.

AROMA-VOC Analyzer Can Detect Specific VOCs

- AROMA can measure part-per-trillion, speciated VOC measurements in near real-time.
- It has been developed and validated for a range of VOCs in environmental gas samples.
- It has been used to measure VOCs in sanitary sewer headspace.
- It has also been used to monitor alcohol and fluoroalcohol tracers in produced oilfield fluid.
- AROMA is designed for long-term, continuous operation in harsh environments.

Project Goal and Approach

Implement a near real-time VOC analyzer to detect specific VOCs at low detection limits (µg/L - ng/L) prior to and after treatment for RO- and GAC-based potable reuse applications.

Task 1: VOC Analyzer Method Optimization

Task 2: Validation of the VOC Analyzer

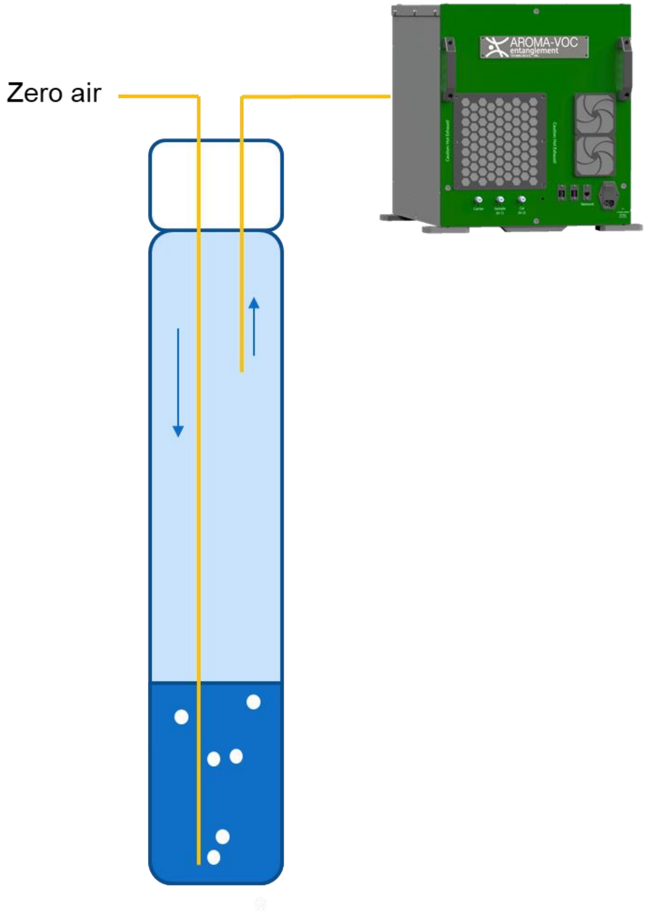
Task 3: Field Testing at Full- and Pilot-Scale Systems

Task 1: VOC Analyzer Method Optimization

Objectives:

1) Extend the capabilities of an existing VOC analyzer to target VOCs of interest in potable reuse.

2) Amend the existing direct sparge interface system for online water sampling.



Selection for Organic Compounds

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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

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

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

Debroux, J., Plumlee, M., Trussell, S. **2021,** Defining Potential Chemical Peaks and Management Options, WRF #4991.

Rejection Does not Necessarily Correlate with Molecular size of an Organic Compound

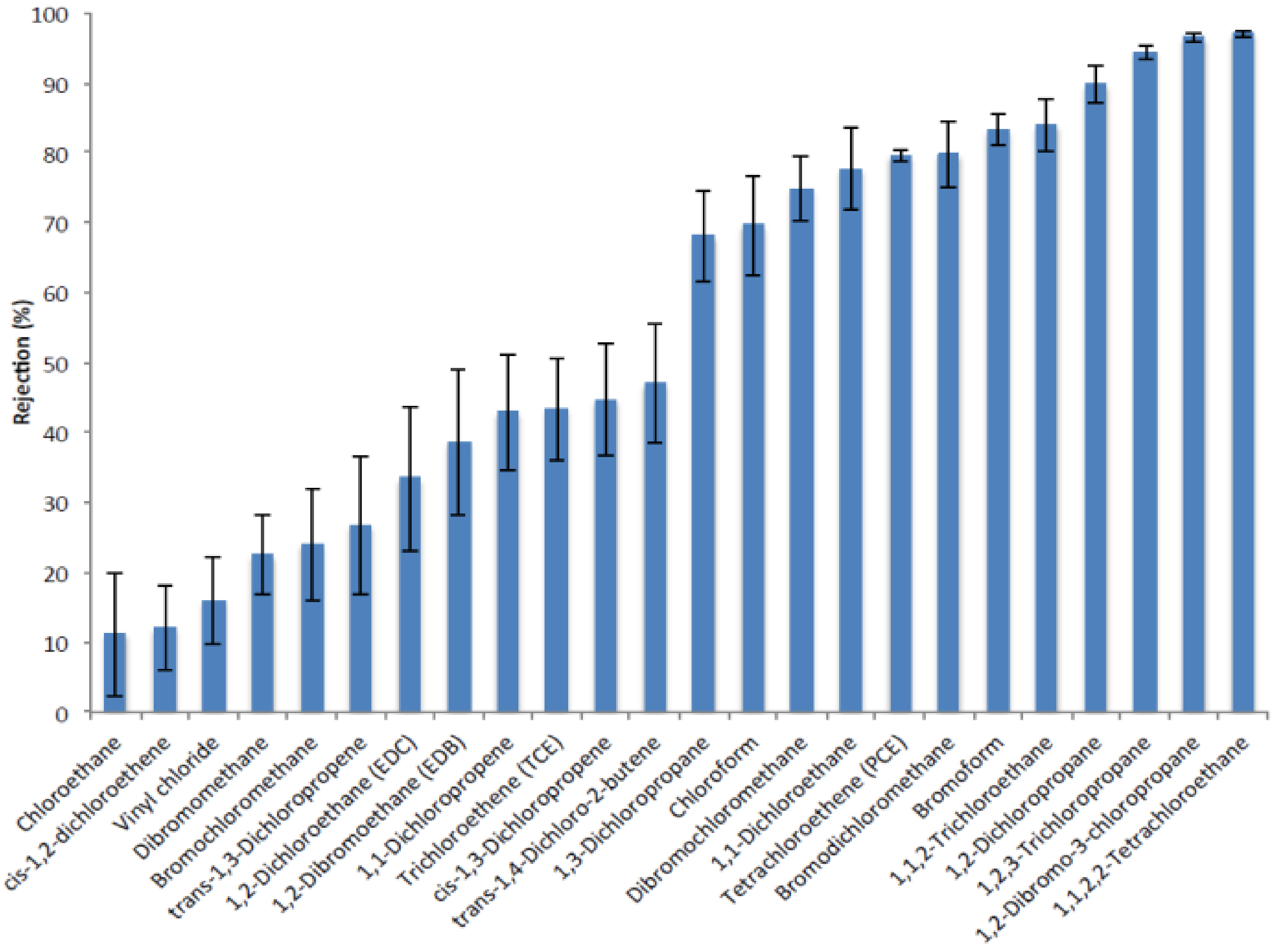

Figure 4-13. Haloalkane and Haloalkene Rejection.

Howe, K.J., Minakata, D., Breitner, L.N., Zhang, M. **2019,** Predicting Reverse Osmosis Removal of Unique Organics, WRF #4769.

Considerations for Selecting Organic Compounds

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(1) Potential for incomplete removal by advanced treatment systems employing RO with UV-AOP.

(2) Health relevant where levels were 10x less than the 100 μg/L limit measured as "TOC"/NPOC.

(3) Potential for non-detection by online purgeable organic carbon analyzers.

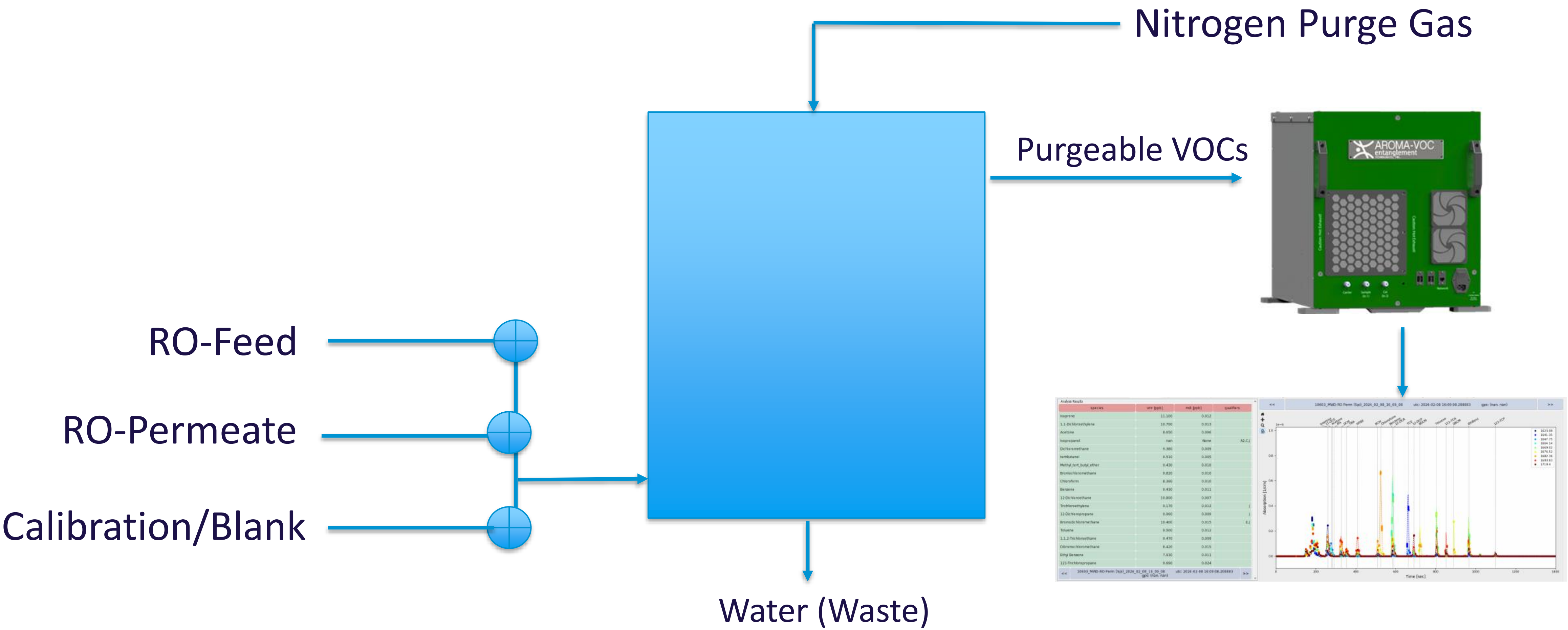
(4) Has already been measured by the AROMA analyzer.

(5) Compounds already detected in RO permeates.

(6) Other compounds considered: NDMA, Formaldehyde, Vinyl Chloride, Methyl Chloride, 1,3-Butadiene, Acrylonitrile.

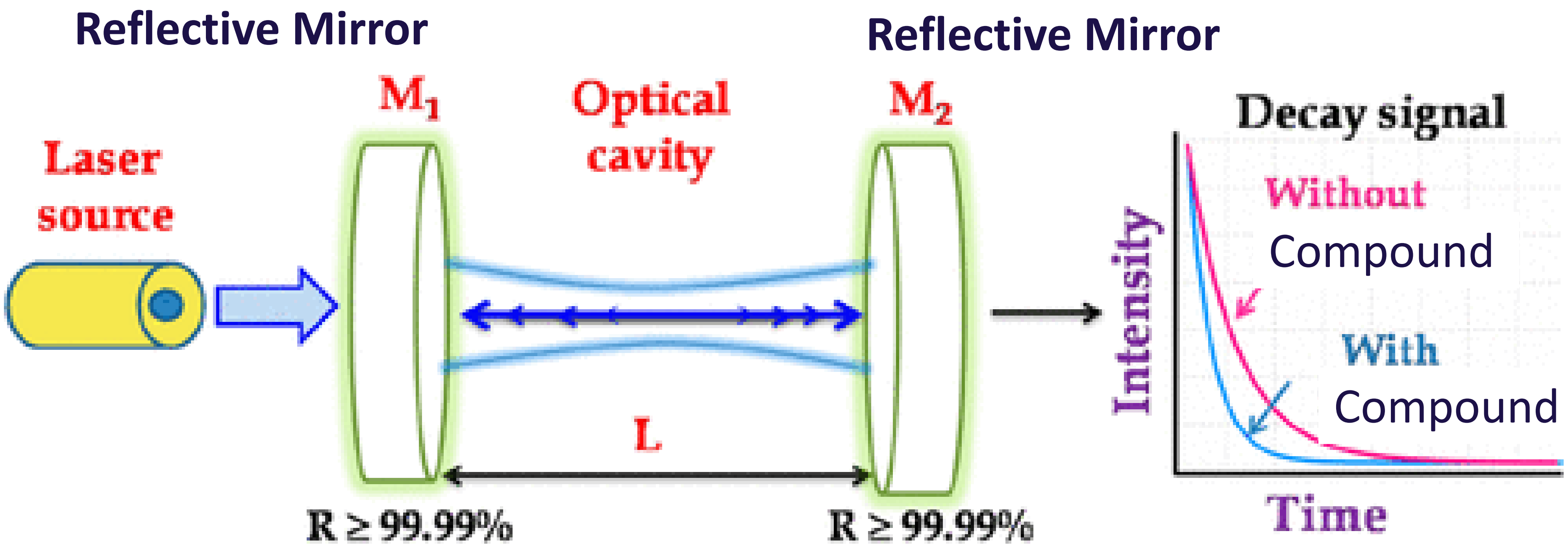
	Compounds	MW (g/mol)	Hyc
1	Tert-Butyl Alcohol	74	3.70E-04
2	Acetone	58	1.40E-02
3	1,2,3-Trichloropropane	147	1.40E-02
4	Methyl Tert-Butyl Ether (MTBE)	88	3.00E-02
5	1,1,2-Trichloroethane	133	3.14E-02
6	Dibromochloromethane	208	3.20E-02
7	1,2-Dichloroethane	99	4.81E-02
8	Bromodichloromethane	163	8.67E-02
9	Bromochloromethane	129	1.00E-01
10	1,2-Dichloropropane	113	1.10E-01
11	Methylene Chloride	85	1.20E-01
12	Chloroform	119	1.50E-01
13	1,1-Dichloroethane[a]	99	2.00E-01
14	Benzene	78	2.27E-01
15	Toluene	92	2.69E-01
16	1,1,2-Trichloroethylene	131	3.10E-01
17	Ethylbenzene	106	3.14E-01
18	1,1-Dichloroethene	97	1.00E+00
19	Isoprene	68	2.19E+00

Continuous Dynamic Headspace Apparatus



General flow diagram of the optimized direct sparge interface for online analysis of VOCs from water

Cavity Ring-Down Laser Absorption Spectroscopy



Maity et al. Anal. Chem. **2021**, 93, 1, 388−416

Measurements are Dependent on Specific Wavelengths

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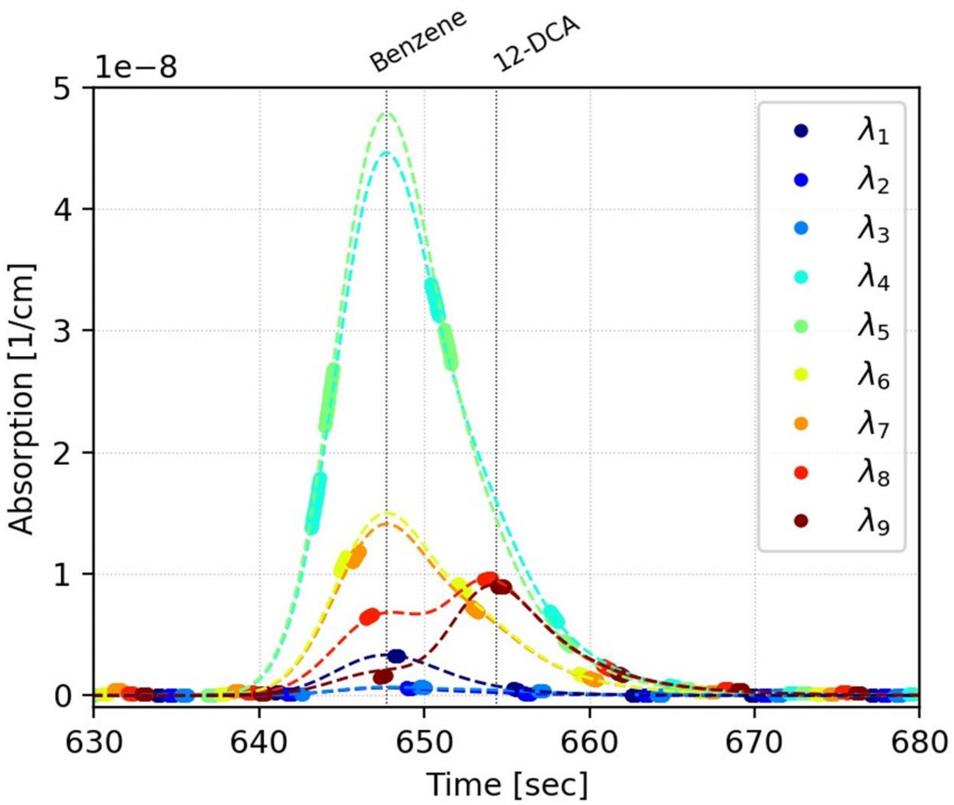
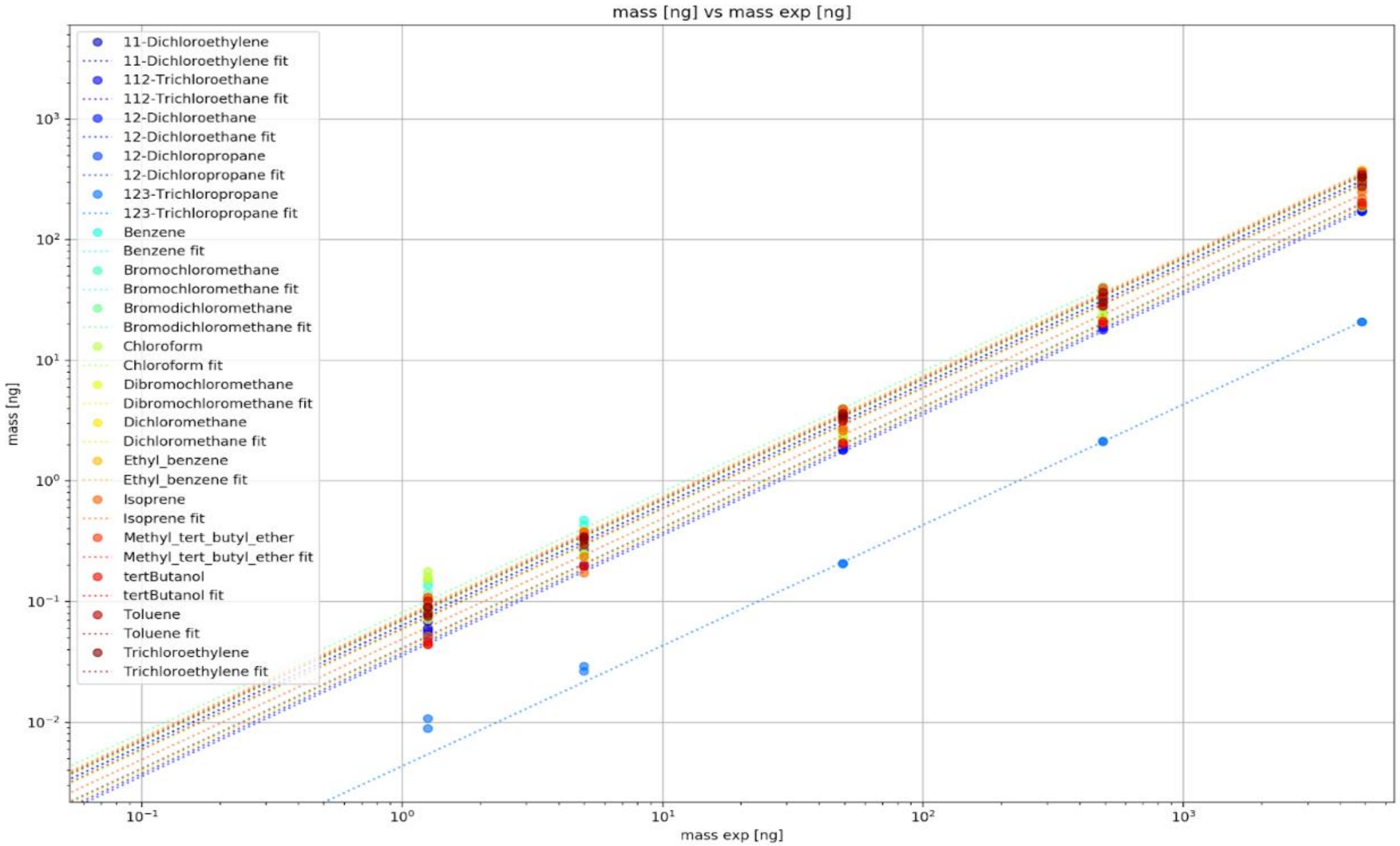


- A column is used for chromatographic separation and laser absorption spectroscopy is used for detection.
- Elution trace of benzene and 1,2-dichloroethane (1,2 DCA) spiked at 130 ng/L in RO permeate sparged with ultra-high purity nitrogen measured at various wavelengths.
- Method developed for 19 VOC compounds (~50 minute method).

Developed Calibration Curves



- Relative standard error (RSE) for all of the data points used for calibration were below +/- 30 %.
- R square values of all calibrated compounds > 0.99
- <u>MDLs range from 10 to 90 ng/L</u>

Task 2: Validation of the VOC Analyzer

<u>Objectives</u>:

1) Externally validate for differing wastewater matrices.

2) Quantify RO rejection performance for the target VOCs.

Evaluate AROMA for Various Wastewater Matrices

- Obtained feed AND effluent/permeate wastewater samples from all participating utilities using RO (7 sites) and GAC (3 sites) processes within potable reuse systems.
- Analysis of 1) ambient and 2) matrix spiked samples
  - Ambient and 65 ng/L, 2 μg/L, 10 μg/L spikes
- Third party laboratory analysis of samples for comparison to the AROMA analyzer (EPA Methods 5030B and 8260B).

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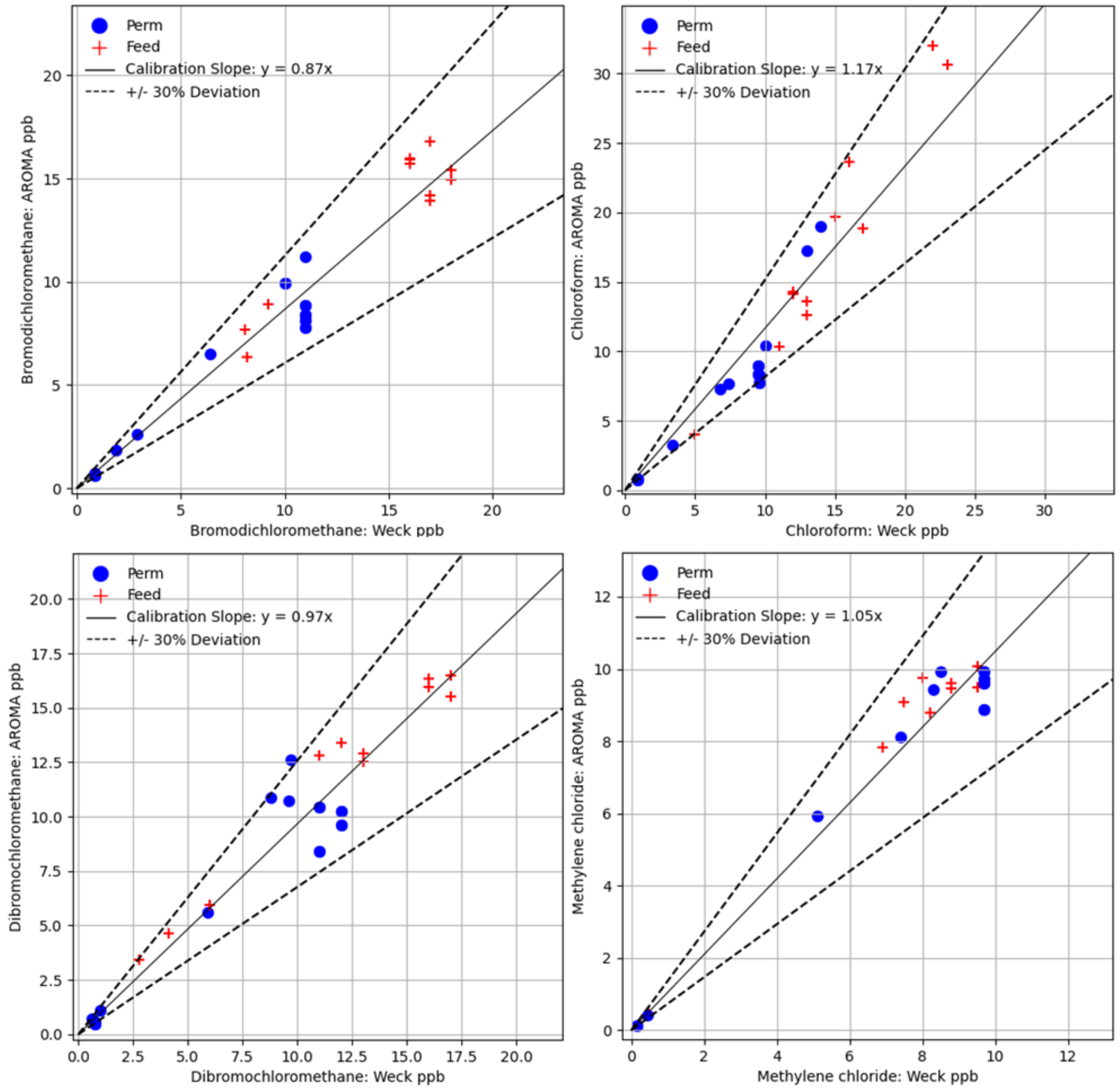
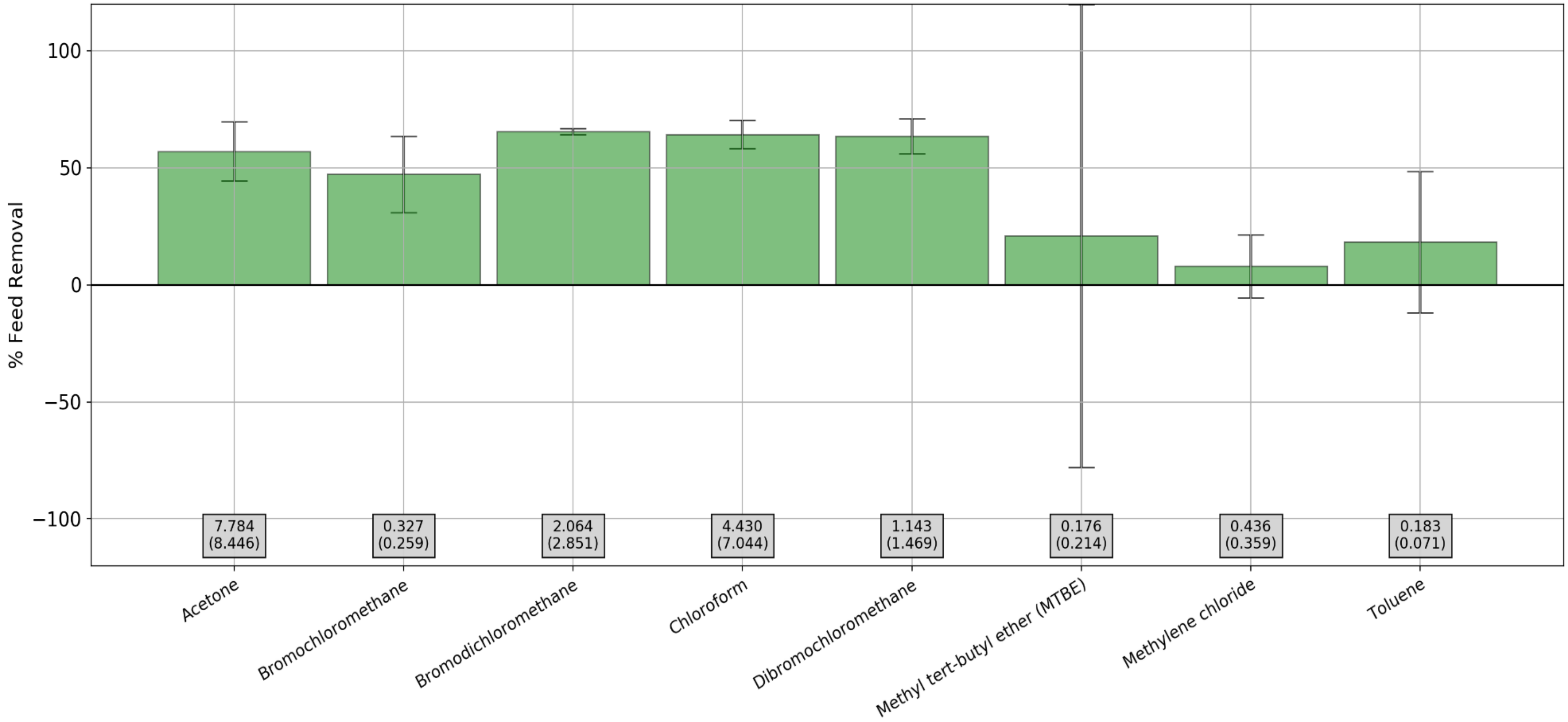
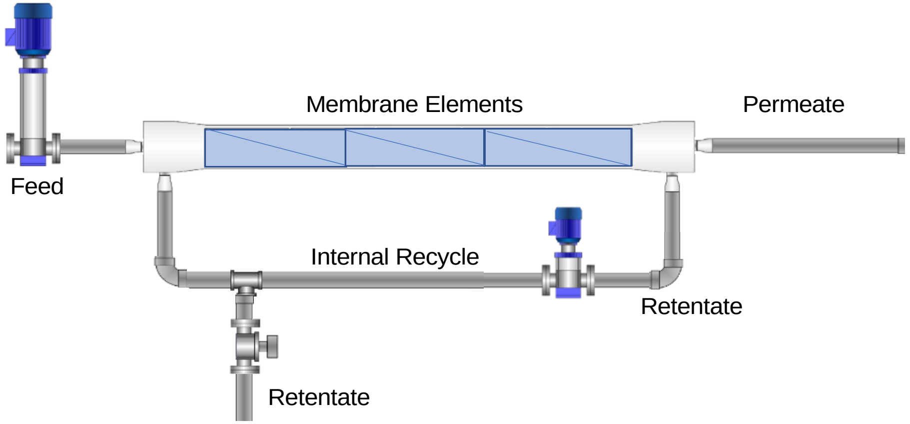
AROMA and EPA Methods are Comparable



VOCs Were Only Partially Removed by Full-Scale RO

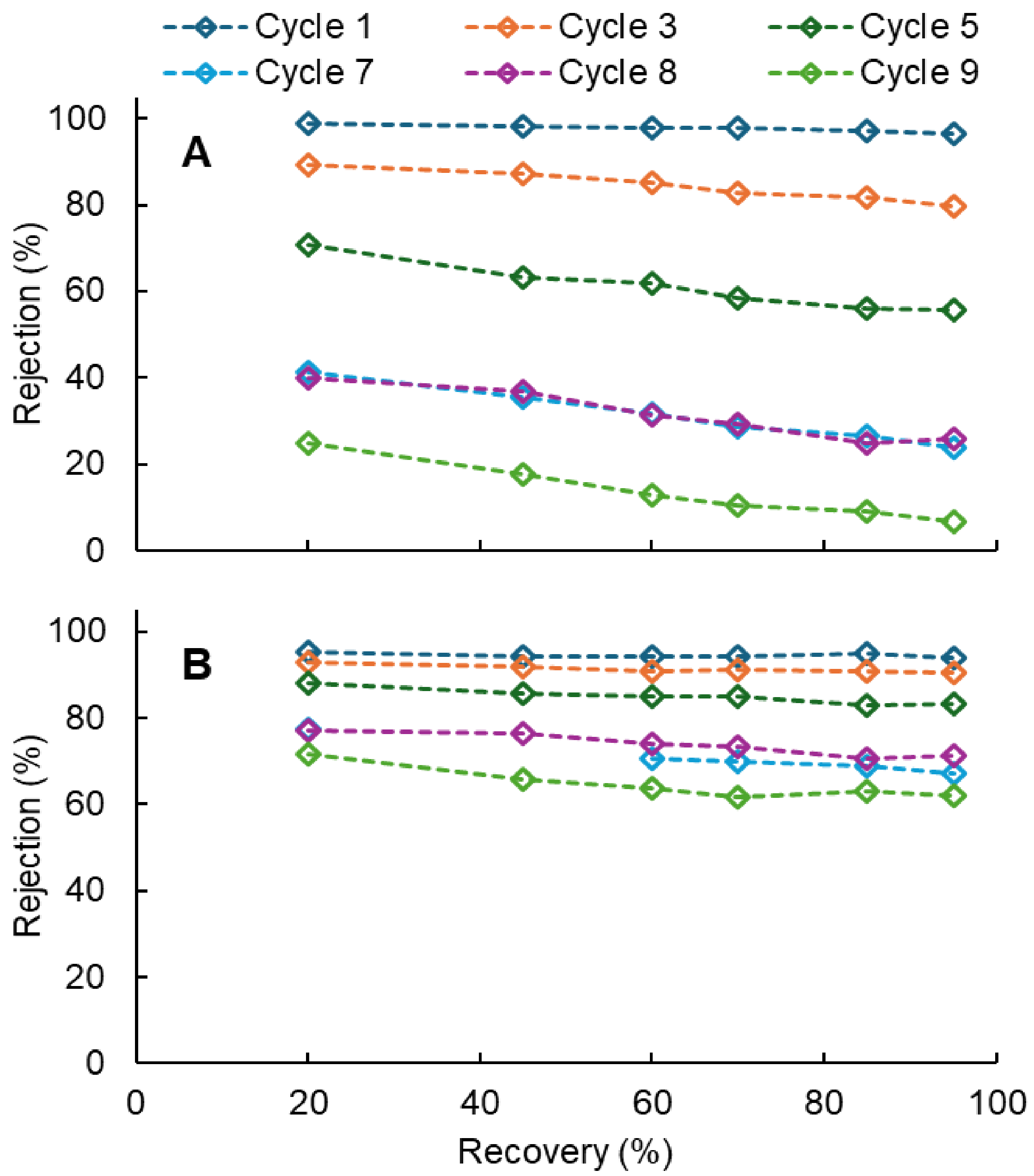


Task 2: Quantify RO Rejection Performance for Spiked VOCs



Colorado School of Mines' Small-Scale Closed Circuit RO system

VOC Rejection Can Be Impacted by Long-Term Operational and Membrane Conditions



Task 3: Field Testing at Full- and Pilot-Scale Systems

Objectives:

1) Verify the feasibility of long-term operation of the VOC analyzer at full-scale

2) Evaluate its performance at pilot-scale with chemical peak simulations

Task 3: Field Testing (*in progress*)

Field Testing at Full- and Pilot-Scale Systems

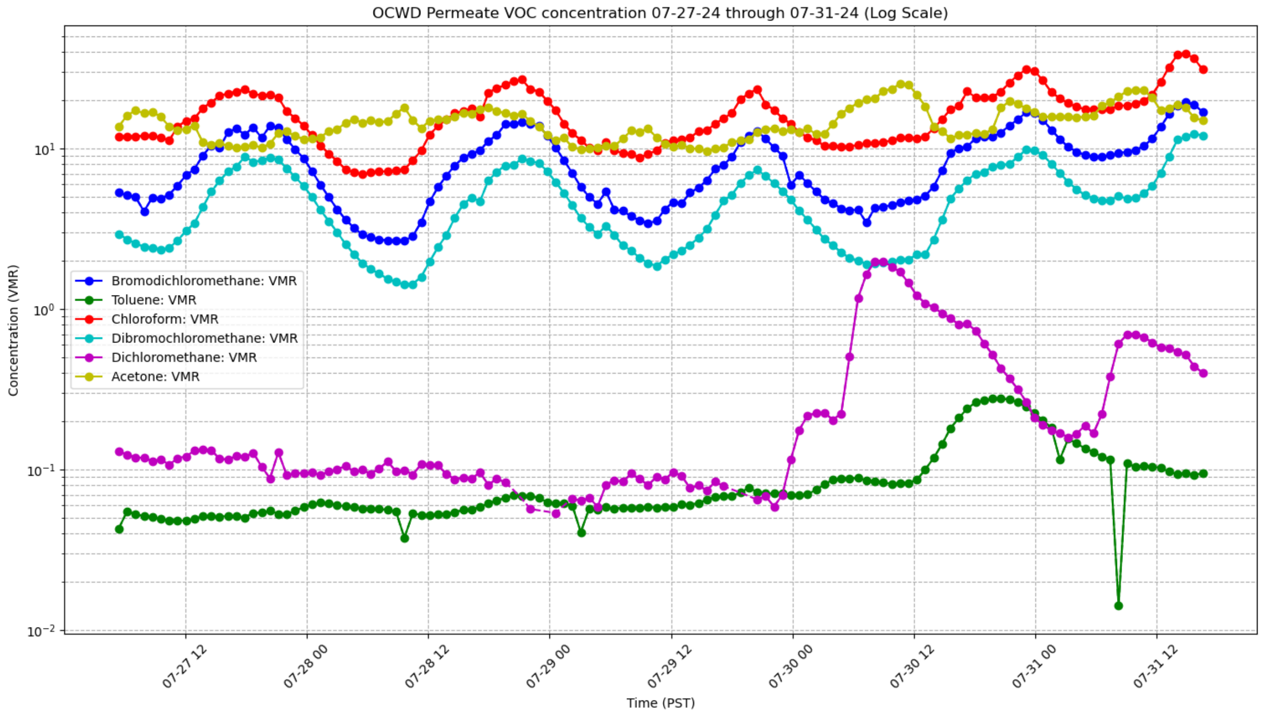
Orange County Water District (OCWD)
Groundwater Replenishment System (GWRS) Reverse Osmosis (RO) Facility

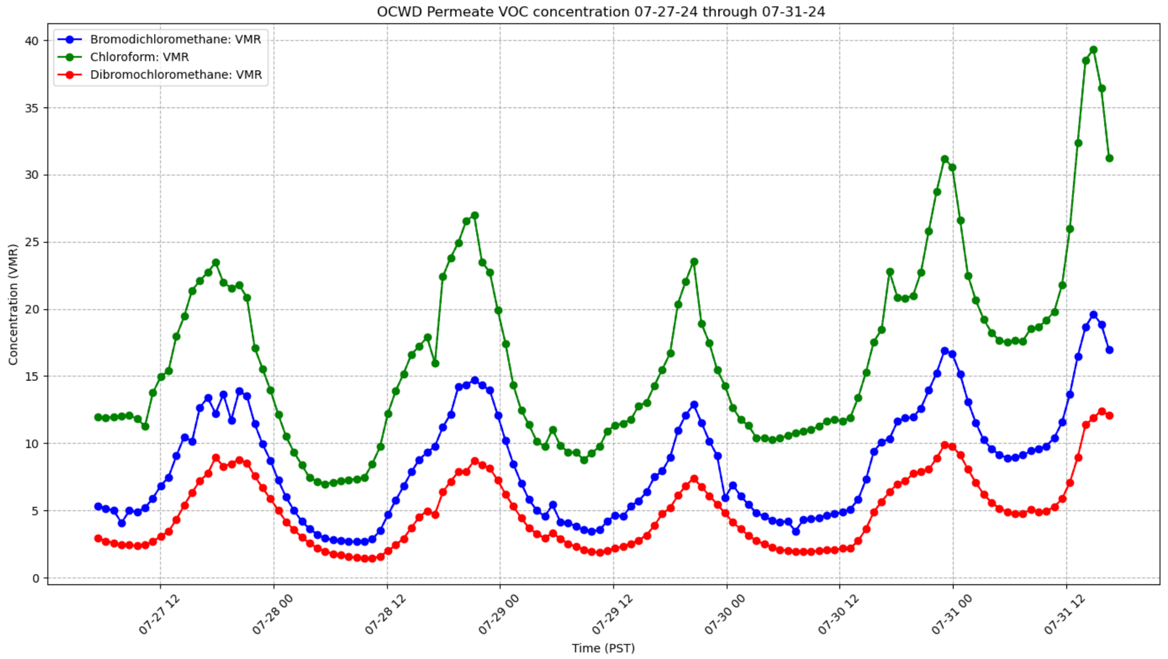
Orange County Water District (OCWD) RO pilot test system

AROMA installed in July 2024 at OCWD GWRS RO Facility

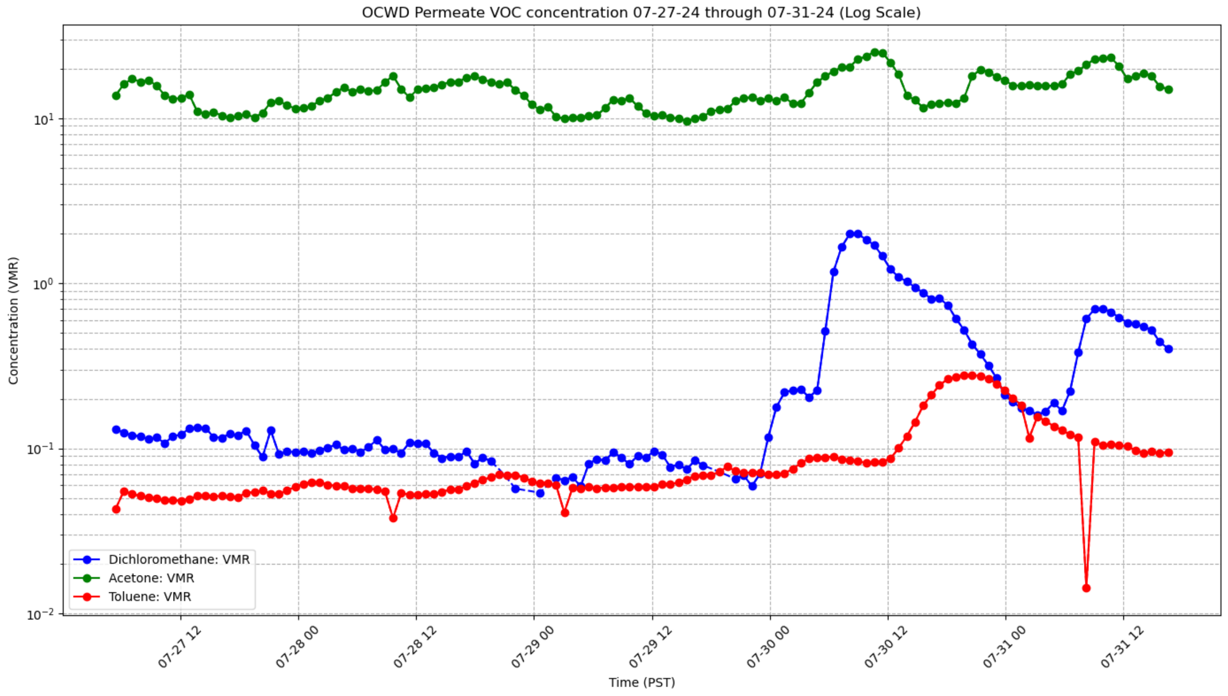
On-Line Monitoring Preliminary Results

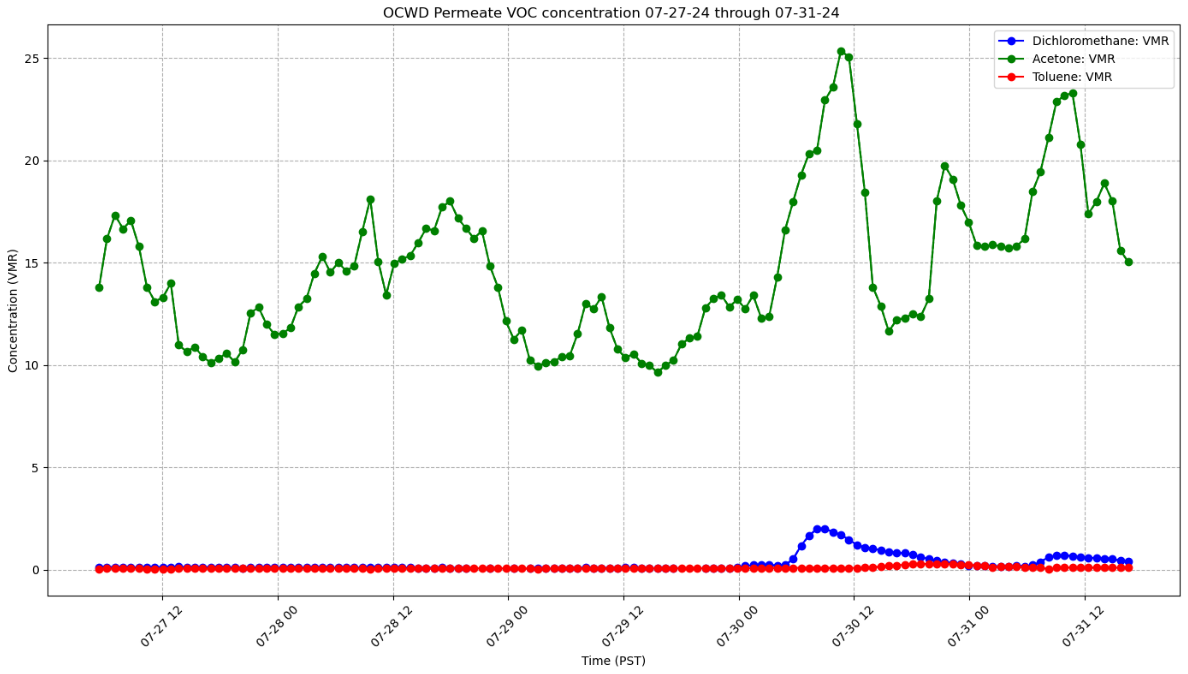
NOTE: Qualitative Results Only! These results are preliminary and have not been validated by 3rd party testing.





On-Line Monitoring Preliminary Results





NOTE: Qualitative Results Only! These results are preliminary and have not been validated by 3rd party testing.

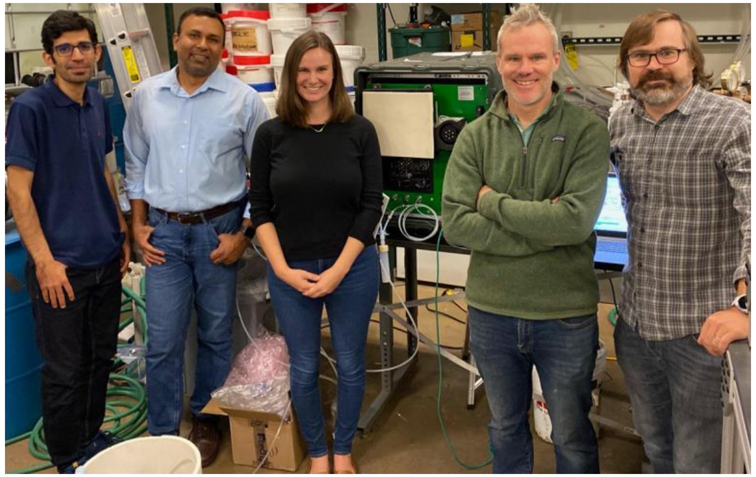
Next Steps

- Compare VOC concentrations and trends to online TOC measurements
- Future Sampling Plan
  - 1 measurement / hour
  - Current trends are showing increases and decreases in concentrations over ~12 hours
- Conduct peak simulations on RO pilot test system
- Compare results with grab samples

VOC Analyzer Can Provide Sensitive Analysis for Specific VOCs

- So far, accurate analysis across water types.
- Be used in tandem with online NPOC (TOC) analyzers.
- Target VOCs that NPOC cannot, like purgeable VOCs or events below the NPOC detection limit.

- Identify VOCs that NPOC does detect
- Rule out regulated VOCs if NPOC does detect.



Questions or Comments?

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