Direct Potable Reuse (DPR) Criteria Expert Panel (AB 574)

DPR-4: Treatment for Averaging Potential Chemical Peaks

August 25, 2021

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DPR-4: Treatment for Averaging Potential Chemical Peaks

- Full advanced treatment (MF/RO/UV-AOP) is a highly effective treatment train employed today for groundwater recharge
- Water quality excursions have been observed

Acetone

\[
\text{CH}_3\text{C} = \text{O} \\
\text{CH}_3
\]
What is a chemical peak?

- Diurnal and process-related TOC baseline variations
- Outliers
Defining a chemical peak

• Peak height – must exceed baseline threshold
  • Due to outliers, non-normal distribution
  • All data used
  • Baseline Threshold = Q3 + 1.5 * IQR, where IQR = Q3 - Q1

• Peak width – Due to non-plug flow processes and recycle flows in WWTP, an instantaneous illicit discharge results in a peak width of hours to days
  • On-line data every 15 minutes
Example excursions from baseline
What chemicals can pass through FAT?

Summary of RO rejection of organic compounds and chemical families

<table>
<thead>
<tr>
<th>Chemical Family</th>
<th>Sub-group</th>
<th>Good (&gt;90%)</th>
<th>Intermediate (50-90%)</th>
<th>Poor (&lt;50%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>VOCs</strong></td>
<td>Solvents and Industrial Compounds</td>
<td>Ethers</td>
<td>Halobenzenes; 1,1,2-TCE</td>
<td>Nitriles; Haloalkenes</td>
</tr>
<tr>
<td></td>
<td>Haloalkanes</td>
<td>CCl₄; Ethanes with 3-4 Cl atoms; Most C₄⁺ haloalkanes</td>
<td>Some C₁-C₃ haloalkanes</td>
<td>C₁-C₂ haloalkanes with 1-2 halogen atoms</td>
</tr>
<tr>
<td></td>
<td>Alkylbenzenes</td>
<td>C₁₀⁺</td>
<td>C₆-C₉</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pesticides/Herbicides</td>
<td>1,2,3-TCP</td>
<td></td>
<td>MITC</td>
</tr>
<tr>
<td><strong>LMW Oxygenated Compounds</strong></td>
<td>Alcohols</td>
<td>Branched C₄⁺ alcohols</td>
<td>Isopropyl alcohol; Most unbranched alcohols</td>
<td>Methanol; Ethanol;</td>
</tr>
<tr>
<td></td>
<td>Aldehydes, Ketones</td>
<td>Methyl isobutyl ketone (MIBK)</td>
<td>Acetone; Most Ketones</td>
<td>Formaldehyde; Most Aldehydes</td>
</tr>
<tr>
<td><strong>PPCPs</strong></td>
<td>Flame Retardants</td>
<td>Chlorophosphates; PFAS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pharmaceuticals</td>
<td>Steroids; β-blockers; NSAIDs; X-ray Contrast Media</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>DBPs</strong></td>
<td>Nitrosamines</td>
<td>C₄⁺ nitrosamines; NMOR</td>
<td>NDMA; NDEA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Halogenated DBPs</td>
<td>HAAs</td>
<td>HANs</td>
<td>THMs</td>
</tr>
</tbody>
</table>

### Predicted removal of organic compounds via AOP

<table>
<thead>
<tr>
<th>Family</th>
<th>Greater than 1,4-dioxane</th>
<th>Less than 1,4-dioxane</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>Haloalkenes</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt; Haloalkanes</td>
</tr>
<tr>
<td></td>
<td>Halobenzenes</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt; Alcohols</td>
</tr>
<tr>
<td></td>
<td>Alkylbenzenes</td>
<td>C&lt;sub&gt;1&lt;/sub&gt;-C&lt;sub&gt;3&lt;/sub&gt; Aldehydes</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;4&lt;/sub&gt;+ Alcohols</td>
<td>C&lt;sub&gt;3&lt;/sub&gt;-C&lt;sub&gt;5&lt;/sub&gt; Ketones</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;4&lt;/sub&gt;+ Aldehydes</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td></td>
<td>C&lt;sub&gt;6&lt;/sub&gt;+ Ketones</td>
<td>MITC</td>
</tr>
<tr>
<td></td>
<td>Acrylonitrile</td>
<td></td>
</tr>
<tr>
<td>PPCPs</td>
<td>Most pharmaceuticals</td>
<td>Flame Retardants</td>
</tr>
<tr>
<td>DBPs</td>
<td>Nitrosamines&lt;sup&gt;1&lt;/sup&gt;</td>
<td>THMs</td>
</tr>
</tbody>
</table>

Notes: 1. High removal in UV/AOP systems

### Organic compounds poorly removed by FAT

<table>
<thead>
<tr>
<th>Family</th>
<th>Compounds poorly removed by FAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>LMW haloalkanes</td>
</tr>
<tr>
<td></td>
<td>LMW alcohols, aldehydes, ketones</td>
</tr>
<tr>
<td></td>
<td>Acetonitrile</td>
</tr>
<tr>
<td></td>
<td>MITC</td>
</tr>
<tr>
<td>DBPs</td>
<td>THMs</td>
</tr>
</tbody>
</table>
Potential Treatment/Blending Technologies

- Ozone/BAC Pre-treatment
- Additional RO/AOP Treatment
- Air Stripping
- Blending
- Activated Carbon
Case Studies

• Compare elements of source control measures, experiences, monitoring and detection of chemical peaks
  • Orange County Water District Ground Water Replenishment System
  • Singapore Public Utilities Board
  • City of San Diego North City Pure Water Demonstration Facility

• Compare strategies for averaging Chemical Peaks
TOC and Acetone grab sample results during 2013 GWRS Acetone event

<table>
<thead>
<tr>
<th>Sample Date</th>
<th>Sample Location</th>
<th>EPA 524.2 Acetone</th>
<th>Theoretical TOC from Acetone</th>
<th>EPA 415.3 TOC</th>
<th>Baseline TOC</th>
<th>Acetone Contribution to Elevated TOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2/18/2013 6:00AM</td>
<td>RO Feed</td>
<td>1,940 µg/L</td>
<td>1.2 mg/L</td>
<td>9.39 mg/L</td>
<td>~ 8.0 mg/L</td>
<td>~ 86%</td>
</tr>
<tr>
<td></td>
<td>RO Permeate</td>
<td>1,410 µg/L</td>
<td>0.9 mg/L</td>
<td>1.18 mg/L</td>
<td>~ 0.025 mg/L</td>
<td>~ 78%</td>
</tr>
</tbody>
</table>

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 $\frac{1.2 \text{ mg/L}}{9.39 \text{ mg/L} - 8.0 \text{ mg/L}} = 86\%$)
OCWD TOC monitoring October 24, 2018 acetone event
Singapore PUB

Legend

- High risk
- Business Park

KWRP (34 MGD)

JWPR (45 MGD)

KWRP catchment

UPWRP (79 MGD)

CWRP (202 MGD)
### List of Prohibited Organic Compounds (PUB)

<table>
<thead>
<tr>
<th>Compound</th>
<th>PUB</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2,4-Trimethylbenzene</td>
<td>Furan</td>
<td>Octane</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>Heptane</td>
<td>Polybrominated diphenyl ether</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>Hexane</td>
<td>Styrene</td>
</tr>
<tr>
<td>Benzene</td>
<td>Isobutanol</td>
<td>Tetra-chloromethane</td>
</tr>
<tr>
<td>Decane</td>
<td>Isopropyl ether</td>
<td>Tetra-chloroethylene</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>Methyl ethyl ketone</td>
<td>THF (Tetrahydrofuran)</td>
</tr>
<tr>
<td>Dimethyl sulphide</td>
<td>Methyl isobutyl ketone</td>
<td>Toluene</td>
</tr>
<tr>
<td>Dimethyl sulphoxide</td>
<td>Methyl tert-butyl-ether</td>
<td>Trichloroethylene</td>
</tr>
<tr>
<td>DMF (N,N-Dimethylformamide)</td>
<td>Methylene chloride</td>
<td>Turpentine</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>Nonane</td>
<td>Xylene (o,m,p)</td>
</tr>
</tbody>
</table>
Singapore PUB VOC Monitoring in the Sewershed

![Graph showing the decrease in high VOC incidents from 2010 to 2015 with an increase in 2011 due to the installation of 10 VOC monitoring devices.](image)

- **No. of high VOC incidents**
- **Year**
San Diego Pure Water Demonstration Facility
Chemical Challenge Testing

• Spike of Acetone, NDMA, Formaldehyde, and 1,4-dioxane into Feed Water
• Evaluate O$_3$ & BAC as additional barrier
• Test removal of O$_3$-BAC-MF-RO-UV/AOP vs. MF-RO-UV/AOP

Formaldehyde ~300 µg/L
Acetone ~2,600 µg/L
1,4-dioxane ~900 µg/L
NDMA ~500 ng/L
Discharge Volume

Tanker full of Acetone (4,500 gal)

55 gal Acetone Drum

1 gal Acetone bottle

TOC (mg/L) vs. Time

10 MG Sewershed

10 MGD WWTP

TOC (mg/L) vs. Time

10 MG Sewershed

10 MGD WWTP

TOC (mg/L) vs. Time

10 MG Sewershed

10 MGD WWTP
Impact of Sewershed Size

Tanker full of Acetone (4,500 gal)

10 MG Sewershed

TOC (mg/L)

Time

10 MGD WWTP

Tanker full of Acetone (4,500 gal)

100 MG Sewershed

TOC (mg/L)

Time

100 MGD WWTP
Chemical Discharge Duration

Tanker full of Acetone (4,500 gal)

1 hour
10 MG Sewershed

Max value 215 mg/L

TOC (mg/L)

Time

Mass under peak ~18,000 lbs

24 hours
10 MG Sewershed

Max value 139 mg/L

TOC (mg/L)

Time

10 MGD WWTP

10 MGD WWTP
Engineered Buffer with Residence up to 24 Hours

CSTR Model Input 2: 10 hr-step at 5.7 mg/L
CSTR Model Input 1: 10 hr-step at 0.9 mg/L

Engineered Buffer Theoretical Retention Time (hours)
- 24
- 12
- 6
- 3

TOC (mg/L) vs Time (hours)

NORI
NATIONAL WATER RESEARCH INSTITUTE

CALIFORNIA WATER BOARDS
Engineered Buffer with Residence up to 60 Days

CSTR Model Input 2: 10 hr-step at 5.7 mg/L

CSTR Model Input 1: 10 hr-step at 0.9 mg/L

CSTR Model Outputs

Engineered Buffer Theoretical Retention Time (days)
- 60
- 30
- 10
- 1

Time (hours)

TOC (mg/L)
How will online TOC analyzers be used?

• Advanced oxidation reactions to mineralize organic carbon in sample (UV/persulfate and O₃/hydroxide)

• Expert panel expressed concern that highly volatile organics might not be captured with online TOC
Experimentation to Evaluate TOC Analyzers

Compounds Considered and Tested:
• Carbon tetrachloride
• Vinyl Chloride
• Toluene
• Carbon Disulfide
• 1,2-dichloropropane
• Methylene Chloride (Dichloromethane)
• Acetone
• Methyl isobutyl ketone
<table>
<thead>
<tr>
<th>*OH rate constant ((k_{*OH}, \text{L/Mol}*s))</th>
<th>Henry's Law Constant ((\text{Hyc}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HYC &gt; 1.0</td>
</tr>
<tr>
<td></td>
<td>0.1 &lt; HYC &lt; 1.0</td>
</tr>
<tr>
<td></td>
<td>0.01 &lt; HYC &lt; 0.1</td>
</tr>
<tr>
<td>(k_{*OH} &gt; 1 \times 10^9)</td>
<td>Vinyl chloride</td>
</tr>
<tr>
<td>(1 \times 10^8 &lt; k_{*OH} &lt; 1\times10^9)</td>
<td>Toluene</td>
</tr>
<tr>
<td>(1 \times 10^7 &lt; k_{*OH} &lt; 1 \times 10^8)</td>
<td>MIBK</td>
</tr>
<tr>
<td></td>
<td>Acetone</td>
</tr>
<tr>
<td></td>
<td>Methylene chloride</td>
</tr>
</tbody>
</table>
## Experimentation to Evaluate TOC Analyzers

<table>
<thead>
<tr>
<th>Round 1 Participants</th>
<th>Model</th>
<th>Instrument Type</th>
<th>Measured Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bench Top</td>
<td>Online</td>
</tr>
<tr>
<td>OCWD</td>
<td>M9 portable</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>City of San Diego</td>
<td>M5310C</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>Shimadzu TOC-L (Low Level)</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Suez</td>
<td>M9 portable</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td></td>
<td>M5310C</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Shimadzu</td>
<td>Shimadzu TOC-L</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Valley Water</td>
<td>M5310C</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Hach</td>
<td>Biotector 3500</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>SNWA</td>
<td>Shimadzu TOC-L</td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>

TOC analyzers demonstrated acceptable performance of measurement of volatile organic compounds (Hyc ≤ 0.133) with at least 50% recovery.
Chemical Control Strategies

- Enhanced Source Control
- Sewershed Monitoring
- NDN + Filters
- O₃/BAC
- Response Time
- Diversions
- Blending
- Dilution
Chemical Control – Public Health Protection

This box represents what is required for public health protection...
Chemical Control – Public Health Protection

Enhanced Source Control
Sewershed Monitoring
NDN + Filters
O₃/BAC
Response Time
Diversions
Blending
Dilution

This box represents what is required for public health protection...

...and there may be many ways to fill this box.
Chemical Control – Balance is Key

- Enhanced Source Control
- Sewershed Monitoring
- NDN + Filters
- O$_3$/BAC
- Response Time
- Diversions
- Blending
- Dilution

Flowchart:
- Dilution

Diagram:
- Advanced Treatment Facility
- Reservoir
- Water Treatment Plant
Chemical Control – Balance is Key

- Sewershed Monitoring
- NDN + Filters
- O₃/BAC
- Response Time
- Diversions
- Blending
- Dilution

- Enhanced Source Control
- NDN + Filters
- O₃/BAC
- Response Time
- Diversion

Advanced Treatment Facility
Reservoir
Water Treatment Plant
People
Chemical Control – Balance is Key

Enhanced Source Control  Sewershed Monitoring  NDN + Filters  O₃/BAC  Response Time  Diversions  Blending  Dilution

Dilution  Response Time

Enhanced Source Control  NDN + Filters  O₃/BAC

Advanced Treatment Facility  Reservoir  Water Treatment Plant

Advanced Treatment Facility
Chemical Control – Balance is Key

Enhanced Source Control | Sewershed Monitoring | NDN + Filters | O₃/BAC | Response Time | Diversions | Blending | Dilution

Dilution | Response Time

Enhanced Source Control | NDN + Filters | O₃/BAC

Diversions | Enhanced Source Control

NDN + Filters | O₃/BAC | Sewershed Monitoring

Advanced Treatment Facility | Reservoir | Water Treatment Plant

Advanced Treatment Facility → People

People
Chemical Control – Equivalence

- Enhanced Source Control
- Sewershed Monitoring
- NDN + Filters
- O$_3$/BAC
- Response Time
- Diversions
- Blending
- Dilution

Dilution
Response Time
Enhanced Source Control
NDN + Filters
O$_3$/BAC

Diversions
Enhanced Source Control
Response Time
NDN + Filters
O$_3$/BAC
Sewershed Monitoring

Advanced Treatment Facility
Reservoir
Water Treatment Plant

Advanced Treatment Facility
DPR-4 Recommendations

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). 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).
DPR-4 Recommendations

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)... 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... 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.
DPR-4 Recommendations

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).
DPR-4: Treatment for Averaging Potential Chemical Peaks

Thank you to:
Research Team: Stephen Timko, PhD, Rodrigo Tackaert, PhD, Aleks Pisarenko, PhD
TWG: Jim Crook, PhD and Adam Olivieri, Dr. PH
PAC: Mehul Patel, PE
Guidance: SWRCB, Water Research Foundation, California DDW