Treatment Options for Emerging Contaminants - What is Happening in North Carolina?
Presentation Outline

- Emerging Contaminants
- What is happening in North Carolina?
- 1,4-Dioxane and PFAS
- Treatment options used for emerging contaminants
- Conclusions
Unregulated compounds that pose a potential negative impact to health and environment:

- Perchlorate
- 1,4 Dioxane
- PFOS & PFOA (HA of 70-ppt) and other PFAS compounds
- DBPs such as Brominated and Iodinated DBPs, Chlorate, Nitrosamines
- Algal toxins, Cr(VI), PPCPs, SOCs, Carcinogenic VOCs, Strontium
- New contaminants are being identified and better understood every year
What is Happening in North Carolina? UCMR3 revealed 1,4 Dioxane and PFAS in Cape Fear River

1,4 Dioxane Detections

PFAS Detections

Source: Joe Mattheis, Eurofins 2016
NCDWR has asked Cape Fear Basin dischargers to test for “Total PFAS” and 1,4 Dioxane and suggest potential actions to limit discharges from POTWs.
Presentation Outline

- What emerging contaminants are of concern?
- What is happening in North Carolina?
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- Conclusions
1,4-Dioxane

- EPA listed as a probable carcinogen
- Highly soluble and mobile in groundwater
- Potentially biodegradable under acclimated aerobic conditions, but not readily biodegraded at most plants
- Does not readily evaporate from surface waters
- 0.3 to 5 ug/L action levels already in place in some states.
- No MCL action near-term for drinking water by EPA or NC
- NC has 0.35 ug/L source water quality standard for drinking water supplies
- NC NPDES permits can include monitoring for 1,4 Dioxane and are starting to include 1,4 Dioxane limits in NPDES Permits
What are PFAS compounds?

- Per- and Polyfluoroalkyl Substances (PFAS) are a large class of manufactured fluorosurfactant chemicals that:
  - have many uses (over 4,000 PFAS compounds in the global market) – used since 1940’s
  - are environmentally persistent (not readily biodegradable) and mobile in the environment
  - have potential human health effects
  - contains very strong carbon-fluorine bonds

PFAS-containing products repel water, grease and stains
PFAS as a family (chain length)

- **Per- and Poly-FluoroAlkyloalkyl Substances (PFAS)**

- **PerFluoroOctanoic Acid (PFOA)**

- **PerFluoroOctaneSulfonic Acid (PFOS)**

USEPA Health Advisory Level (ng/L) 70 (PFOA+PFOS)
GenX Replaced PFOA (C8) in Fluorochemical Manufacturing in 1980, but the Nov 2016 article by Mei Sun et al, then **public health concerns** in 2017 and onward resulted in utilities at the lower end of the Cape Fear River pursuing treatment **without an EPA MCL**

States have had to Act with Regs and Guidance in Absence of EPA MCL’s

- **California**
  - Notification Level: PFOA (5.1 ppt), PFOS (6.5 ppt)
  - Response Level: PFOA (40 ppt), PFOS (10 ppt)

- **Minnesota**
  - PFOA (35 ppt DW/GW)
  - PFOS (27 ppt DW/GW)
  - PFHxS (27 ppt DW/GW)
  - PFBA (7,000 ppt DW/GW)
  - PFBS (3000 ppt DW/GW)

- **North Carolina**
  - GenX (140 ppt DW)
  - PFOA (2000 ppt GW)

- **Texas**
  - PFOA (290 ppt GW)
  - PFOS (560 ppt GW)
  - Individual limits for 10 other PFAS compounds

- **Iowa**
  - PFOA & PFOS (70 ppt Protected GW)

- **New Hampshire**
  - PFOA & PFOS (70 ppt GW)
  - Proposed ppt MCL’s of 12 PFOA, 15 PFOS, 18 PFHxS, 11 PFNA

- **Maine**
  - PFOA & PFOS (70 ppt DW)

- **Massachusetts**
  - Sum of 5 (70 ppt DW)

- **Rhode Island**
  - PFOA & PFOS (70 ppt DW/GW)

- **Connecticut**
  - Sum of 5 (70 ppt DW/GW)

- **New Jersey**
  - PFOA (14 ppt DW)
  - PFOS (13 ppt DW)
  - PFNA (13 ppt DW)

- **New York**
  - 10 ppt PFOA, PFOS

- **Vermont**
  - Sum of 5 (20 ppt DW/GW)

- **New Hampshire**
  - PFOA & PFOS (70 ppt GW)

- **Michigan**
  - PFOA (8 ppt)
  - PFOS (16 ppt)
  - PFNA (6 ppt)
  - PFHxS (51 ppt)
  - PFBS (420 ppt)

- **GenX (370 ppt)**
Presentation Outline

- What emerging contaminants are of concern?
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- Treatment options used for emerging contaminants
- Conclusions
Summary of Technologies for Emerging Contaminants such as PFAS and 1,4 Dioxane

- **Activated Carbon** (GAC&PAC) - PFAS, PPCPs, SOCs, DBPs, Strontium, Algal Toxins
- **Ion exchange** – PFAS, Perchlorate, Cr(VI), DBPs, Strontium
- **Ozone and Advanced oxidation** - DBPs, Algal Toxins, PPCPs, SOCs, 1,4-Dioxane
- **Membranes such as LPRO** for PFAS, PPCPs, SOCs, DBPs, Perchlorate, 1,4 Dioxane, Cr (VI), Algal Toxins, Strontium, Perchlorate
Advanced Treatment Options

- Activated Carbon
- Ion Exchange (IX)
- Ozonation
- UV-Advanced Oxidation Process (UV-AOP)
- Low Pressure Reverse Osmosis (LPRO)
GAC Adsorption

Macroscopic Pores due to Re-agglomeration

Binder Residue

100 microns

Localized Structure
Graphitic Crystallite

Graphite plate

1,000 angstroms

1x10^{-4} mm

1,000X

Source – Calgon Carbon Corporation
Example Emerging Contaminants from UCMR’s Removed with Activated Carbon

- Trace Organic Chemicals such as PFAS compounds and PPCPs - UCMR3
- SOC's, VOC's - UCMR3
- Algal Toxins - UCMR4
- Nitrosamines - UCMR2 (NDMA removal requires bio-acclimation)
This graph shows sample results below the method reporting level (MRL) at 0 ng/L. Prior to 1/11/18, eighteen PFAS were tested for, and starting this date, testing for the full forty compounds began. Of the forty PFAS tested, ten have an MRL below 5 ng/L and remaining thirty have an MRL of 2 ng/L.
Full Scale Plant PFAS Removal with 40-60 ppm Donau Standard Purification WC-800 PAC to Raw Water Prior to Alum Coagulation

Sample results below the method reporting limits (MRL) were approximated at the MRL for these calculations. This graph therefore represents a conservative depiction of removal percentages that may be at or above the levels shown. The MRL for all of these compounds is 2 ng/L with the exception of PFBA, which has an MRL of 5 ng/L.
Example GAC Contactors
Activated Carbon Pros and Cons in Water Treatment

**Advantages**

- Helps remove taste & odor
- Removes most SOCs (including most PPCPs)
- THM & HAA precursor removal
- Lowers \( Cl_2 \) demand
- Post GAC gives extra particulate/ Cryptosporidium removal
- Can be used intermittently – e.g. PFAS spike, algae bloom, T&O event
- Does not generate a brine or concentrate needing disposal
- Does not change chloride-sulfate mass ratio

**Disadvantages**

- O&M cost for reactivation or new GAC
- Need for pumping to add post-GAC contactors
- Release of adsorbed compounds & bacteria
- Limited effectiveness some compounds so important to know all that require removal and what concentrations in and out are needed
- As PAC, limited contact time for adsorption and bio-removal
- High pH when GAC first goes on line and fines require washed out at start-up
- Manganese removal takes time for acclimation/conditioning
Activated Carbon Effectiveness by Compound

**Less Frequent Change-out, so More Cost-effective**

- Taste/odor compounds, Pesticides & SOCs (including most EDCs & PPCPs) ↓
- Most drinking water regulated organic compounds (e.g. not vinyl chloride)
- Most PFAS compounds, particularly those of longer chain (higher MW) like PFOS and PFOA
- Algal Toxins
- THM & HAA precursors ↓ using biofiltration plus adsorption, especially if after ozone
- Cl₂ demand ↓

**Frequent Change-out Required, so Less Cost-Effective (surface water tests)**

- Short-chained PFAS - PFBA, PFPeA, GenX /mono-ether PFECAS, PFMOAA
- Iopromide, Ibuprofen
- Nicotine and Cotinine
- 1,4-Dioxane and perchlorate
- NDMA (cold water – acclimates for bio-removal in warm water)
- TTHMs after formation
- Some VOCs such as vinyl chloride and dichloromethane
GAC across the State of NC

GAC FILTER ADSORBERS
Asheville Mills River WTP, NRWASA, CFPUA, Raleigh, etc.

GAC POST-CONTACTORS
Pender County WTP, Bladen Bluffs WTP, Piedmont Triad (PTRWA), Davidson Water, etc.
Advanced Treatment Options

- Activated Carbon
- Ion Exchange (IX)
- Ozonation
- UV-Advanced Oxidation Process (UV-AOP)
- Low Pressure Reverse Osmosis (LPRO)
Ion Exchange (IX) is used for Removing Charged Compounds

- Perchlorate
- Strontium
- Natural organic matter (NOM-) and Bromide (Br-) to help DBPs
- PFAS by anion exchange
Ion Exchange Resin

- Contained in columns 4 to 5 feet in depth and 3-5 minutes EBCT
- 20 x 50 mesh area of bead-shaped particles – flow distribution
- Generally charged
  - Anionic
    - Exchange for negative ions
    - Charged with hydroxide (OH-) or chloride (Cl-) ions
  - Cationic
    - Exchange for positive ions
    - Charged with hydrogen (H+) or sodium (Na+) ions
Anion Exchange... “Exchanging what?”

Ion Exchange Basics

- PFAS
- Nitrate (NO$_3^-$)
- Natural Organic Matter (NOM)
- Sulfate (SO$_4^{2-}$)
- Bicarbonate (HCO$_3^-$)
Example Pilot Study for IX and GAC (Cary NC)

Pilot Testing Left to Right are Two Ion Exchange Resins and a GAC column
Bench Scale Testing: GAC versus IX

- RSSCT to Expedite Bench Testing in a Controlled Environment
  - Cuts 6-12 month test down to 2 months
- Two (2) GAC media
  - Coal-based vs. coconut-based
- Two (2) AIX resin media
  - Gel vs. Macroporous resins
- GAC followed by AIX
- Impact of chlorine residual on PFAS removal
Example Anion Exchange Resin System

1. Dechlorination Chemical (or salt system if regenerating onsite)
2. Orthophosphate – CSMR Management
3. AIX Vessels
   - Rupture disk vs. Pressure relief valve
4. Bag filters to protect AIX resin bed when needed
5. Indoors or Outdoors
Ion Exchange (IX) Effectiveness and Issues

- Effective for Perchlorate, Cr(VI), Strontium, Natural Organic Matter and Bromide
- Increasing in application for PFAS removal
- Has shown greater effectiveness at removing short-chain PFAS than GAC
- Resin costs more than GAC ($/pound), but less lb needed, so low space needs and life-cycle cost competitive for PFAS
- Can come pre-washed and thus may not require backwashing or rinsing
- Impacts on corrosion control
- Susceptibility to oxidants
- Currently unable to regenerate for PFAS
- Possible competitive exchange with other compounds present in water
Total PFAS Removal – Cary Pilot

Total Detected PFAS (ng/L)

- Raw Water
- Filter Effluent
- RO
- Post-GAC
- Calgon IX
- Purolite IX

August 8th, 2018
August 20th, 2018
October 18th, 2018
Ion Exchange across the State of NC

Coastal
Anion Exchange for Bromide, Organics/DBP precursors;
Cation exchange for softening—e.g. Aqua

Piedmont
Miex for organics/DBP precursors at Johnston Co and Roxboro

Source - IXOM
Advanced Treatment Options

- Activated Carbon
- Ion Exchange (IX)
- Ozonation
- UV-Advanced Oxidation Process (UV-AOP)
- Low Pressure Reverse Osmosis (LPRO)
Ozone and Advanced Oxidation Process are effective for:

- DBP precursors
- 1,4 Dioxane
- Algal toxins
- Many PPCPs
- Many SOCs

Advanced Oxidation Process:

- Ozone-Peroxide
- UV-Peroxide
- UV-Chlorine
1,4 Dioxane Removal – Cary Pilot

Detected 1,4-Dioxane

Sample Date

August 20th, 2018

August 21st, 2018

October 19th, 2018

1,4-Dioxane Concentration (µg/L)

Raw Water
Filter Effluent
RO
Post-GAC
Calgon IX
Purolite IX
Ozone and Advanced Oxidation Process (AOP) across the State of NC

**Ozone**
- Raleigh
- Cary/Apex
- Asheville
- GUC
- Cape Fear PUA

**AOP**
Numerous temporary installations for 1,4 Dioxane and other groundwater contamination cleanup
Advanced Treatment Options

- Activated Carbon
- Ion Exchange (IX)
- Ozonation
- UV-Advanced Oxidation Process (UV-AOP)
- Low Pressure Reverse Osmosis (LPRO)
## Membrane Operating Conditions

<table>
<thead>
<tr>
<th>Membrane Type</th>
<th>Flux (L/m²/hr)</th>
<th>Pressure Drop (psi)</th>
<th>Size Exclusion (microns)</th>
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<tbody>
<tr>
<td>Microfilter</td>
<td>100-400</td>
<td>5-15</td>
<td>0.1-1</td>
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<td></td>
<td></td>
<td></td>
<td>Crypto/Giardia</td>
</tr>
<tr>
<td>Ultrafilter</td>
<td>100-400</td>
<td>10-30</td>
<td>0.01-0.1</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Viruses</td>
</tr>
<tr>
<td>Nanofilter</td>
<td>30</td>
<td>80-120</td>
<td>0.001-0.01</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Organics (TOC)</td>
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<tr>
<td>Reverse Osmosis</td>
<td>20</td>
<td>125-1200</td>
<td>0.0001-0.001</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Salinity</td>
</tr>
</tbody>
</table>
Reverse Osmosis and Nanofiltration use Spiral Wound Thin Film Composite Membranes
Example RO or NF Plants – Modules of Membranes in Pressure Vessels
Example RO or NF Plant – Cartridge Filters on Right
Installed Cartridge Filters
Example RO or NF Plant – Chemical Cleaning System
Example RO or NF Plant
LPRO Pilot Testing Example – Brunswick Co. NC

- 12-Month Pilot, started February 2018
- Feed Water in Pilot Unit is Filter Effluent
- Four sampling events
- Lab results from February 26, 2018 sampling
  - Gen X = ND
  - Nafion Byproduct 1 = ND
  - Nafion Byproduct 2 = ND
  - PFMOOA = ND
  - All other PFAS = ND
## LPRO Pilot – Example PFAS Test Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Filtered Water Concentration</th>
<th>RO Treated Water</th>
<th>Calculated Removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gen X</td>
<td>7 – 12 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Nafion Byproduct 1 &amp; 2</td>
<td>ND</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>PFMOAA</td>
<td>320 – 750 ng/L</td>
<td>ND – 11 ng/L</td>
<td>98%+</td>
</tr>
<tr>
<td>PFO2HxA</td>
<td>12 – 26 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>PFHxA</td>
<td>19 – 20 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>PFPeA</td>
<td>16 – 17 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>PFOS + PFOA</td>
<td>26 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Sum (45) of PFAS Tested</td>
<td>423 – 892 ng/L</td>
<td>ND – 11 ng/L</td>
<td>--</td>
</tr>
</tbody>
</table>

*All PFAS compounds sampled for have been below detection limits, with the exception of PFMOAA, which was detected up to 11ng/L in 2 of 4 samples*
# LPRO Pilot – Example Test Results

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Filtered Water Concentration</th>
<th>RO Treated Water</th>
<th>Calculated Removal %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4-Dioxane (industrial chemical)</td>
<td>3.2 µg/L</td>
<td>0.2 µg/L</td>
<td>94%</td>
</tr>
<tr>
<td>Carbamazepine (seizure medicine)</td>
<td>13 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Atrazine (herbicide)</td>
<td>58 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Cotinine (metabolite of nicotine)</td>
<td>15 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>DEET (insect repellant)</td>
<td>44 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Simazine (herbicide)</td>
<td>57 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
<tr>
<td>Tris (1,3 dichloro-2-propyl)phosphate (pesticide, flame retardant)</td>
<td>120 ng/L</td>
<td>ND</td>
<td>--</td>
</tr>
</tbody>
</table>
Presentation Outline

▪ What emerging contaminants are of concern?
▪ What is happening in North Carolina?
▪ 1,4-Dioxane and PFAS
▪ Treatment options used for emerging contaminants
▪ Conclusions
Conclusions

- GAC removes many SOCs, PPCPs, PFAS, DBPs, regulated organic contaminants
- Biofiltration and long contact times can greatly increase GAC life and hence cost-effectiveness for many compounds
- Some Activated Carbon’s are much better than others for certain compounds
- Some organic compounds are less well-adsorbed (e.g. 1,4-Dioxane)
- Some poorly adsorbed compounds, like NDMA are more biodegradable on BAC with acclimation
- Ion Exchange can be very effective for the removal of charged compounds (anions and cations) including many short chain PFAS
Conclusions

- Ozone and AOP can provide good removal of DBP precursors, 1,4 Dioxane, and many PPCPs/SOCs.
- Ozone should generally be followed by biofiltration to remove biodegradable organics.
- Reverse Osmosis provides the greatest removal of most contaminants, but generally costs more than GAC, IX or Ozone/AOP individually.
- Bench or Pilot Testing is needed to assess site-specific removals and for accurate alternatives analysis costing.
- Health-effects information and regulatory guidance/action is needed for short-chain PFAS.
- As new contaminants are found, and expectations by regulators and the public increase, use of advanced treatment is increasing.
Advanced Treatment Examples in North Carolina

- PAC for PFAS - Cary and Greensboro (both temporary)
- PAC for DBPs, T&O - Numerous Utilities
- GAC for PFAS, DBPs - Pender Co., LCFWASA, CFPUA
- GAC for DBP Precursors/Adsorptive Removal of SOCs, etc. - NRWASA, Asheville, Piedmont Triad, Raleigh, etc.
- Ion exchange - Many small GW Fixed Bed Resin systems, Two Miex pre-treatment systems (Johnston Co., Roxboro) for DBPs, ion removal
- Advanced oxidation - Remediation Sites for 1,4 Dioxane, etc.
- Ozone – Raleigh, Cary, CFPUA, GUC
  Asheville – for oxidation, DBPs, T&O, Disinfection, some 1,4 Dioxane oxidation
- RO – Over 30 in NC, mostly coastal, 9 over 1 mgd, helps remove all emerging contaminants
Questions?

Water Partnership with CDM Smith

Bill Dowbiggin
919-623-7964
dowbigginwb@cdmsmith.com

Find more insights through water partnership at cdmsmith.com/water and @CDMSmith
Installed RO/NF Membranes
Example 2-1 Stage Array

Cross-Flow (spiral wound or HF)

2-1 Stage Array

- 3 pressure vessels (PV) per array
- 6 elements/PV
- Diameter of element = 20 cm
- 32.5 m² membrane/element
- Water flux = 27 L/m²/hr

Flow rate/element:
- \(\frac{27 \text{ L/m}^2/\text{hr} \times 32.5 \text{ m}^2}{9.8 \times 10^3 \text{ L/hr}} = 9.8 \times 10^3 \text{ L/hr}\)

Flow rate/array:
- \((9.8 \times 10^3 \text{ L/hr}) \times 6 \times 3 = 1.5 \times 10^4 \text{ L/hr}\)
### EPA BAT for Regulated Drinking Water Organic Contaminants

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>GAC</th>
<th>PTA</th>
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<tbody>
<tr>
<td>Alachlor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aldicarb</td>
<td></td>
<td></td>
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<tr>
<td>Aldicarb sulfone</td>
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<td></td>
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<tr>
<td>Aldicarb sulfoxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbofuran</td>
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<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
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</tr>
<tr>
<td>Chlordane</td>
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<td></td>
</tr>
<tr>
<td>Dactapion</td>
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<td></td>
</tr>
<tr>
<td>2,4-D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Di (2-ethylhexyl) adipate</td>
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<td>Di (2-ethylhexyl) phthalate</td>
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<tr>
<td>Dichloromethane</td>
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<tr>
<td>Dichloroethylene</td>
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<td>Dieldrin</td>
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<td>Dieldrin</td>
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<td>Ethylene Dibromide (EDB)</td>
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<td>Lindane</td>
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<tr>
<td>Methoxychloribenzene</td>
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<tr>
<td>Monochlorobenzene</td>
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<tr>
<td>Oxamyl (Vydate)</td>
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<tr>
<td>Pentachlorophenol</td>
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<tr>
<td>Picloram</td>
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<tr>
<td>Polychlorinated biphenyls (PCB)</td>
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<tr>
<td>Simazine</td>
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<td>Styrene</td>
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<tr>
<td>2,3,7,8-TCDD (Dioxin)</td>
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</tr>
<tr>
<td>Tetrachloroethylene</td>
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<tr>
<td>Toluene</td>
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<tr>
<td>Trichloroethylene</td>
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<tr>
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<td>Xylene</td>
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Source: 40 CFR Ch. I (7-1-03 Edition)