Emerging Contaminants – a Primer

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CTO newterra
We live in a very complex world, with hundreds if not thousands of new products and compounds that enter the market each year for either personal, commercial, military or industrial use.

In total they represent millions of tons of manmade substances that in some form may make their way into the world’s most precious resource … our water.

The impact of many of those products and substances are only now being understood by scientists and the medical community around the world.

In fact, testing for many of these compounds is not required to certify water safe for drinking, nor are most of them on the regulated list for drinking water standards.
What are Emerging Contaminants

Substances of emerging concern or emerging knowledge …

New information is being published relating to toxicity of a well known substance.

New observations in the environment that may be attributable to an effluent or substance.

New chemicals on the market in consumer / commercial / industrial products/processes have known or suspected adverse effects.

New routes of exposure in the food web, or a new pathway to humans that is alarming.
Where are Emerging Contaminants

- Wastewater effluents
- Industrial contamination of soil/groundwater
- Landfill leachates
- Airport fire fighting training facilities

*They are in our food, products, consumer goods, water*
Why are they important now?

Just beginning to understand effects on the ecosystem and humans

Were unable to measure or quantify before at ppb or ppt levels

Emerging from contained areas (landfills, airports etc) and into groundwater sources
Emerging Contaminants

Pharmaceuticals

Personal Care Product (PPCP)

Endocrine Disruptors (EDC)

Engineered Nano Particles (ENP) and Microplastics
Pharmaceuticals

Human and veterinary drugs

Dietary supplements
Pharmaceuticals

Excretion by humans and domestic animals

Disposal of unneeded or expired PPCPs by flushing them down a toilet or drain

Discharge from municipal sewage systems or private septic systems. Municipal wastewater treatment plants generally don’t treat for the compounds found in PPCPs.

They can be spread to farmers fields via manure or human waste spreading, then washed into streams or seep into the aquifer
Some of the ingredients in beauty products just aren’t that pretty.

One in eight of the 82,000 ingredients used in personal care products are industrial chemicals:
  - carcinogens
  - pesticides
  - reproductive toxins
  - hormone disruptors.

Compounds from cosmetics, lotions and sunscreen enter surface water bodies through direct contact or through discharge from STP.
Cosmetics

BHA and BHT
Coal tar dyes
DEA-related ingredients
Dibutyl phthalate
Formaldehyde-releasing preservatives
Parabens
Parfum (a.k.a. fragrance)
PEG compounds
Petrolatum
Siloxanes
Triclosan
Cosmetics – emerging Siloxanes

Siloxanes, also known as silicones, are manmade saturated silicone-oxygen hydrides and are listed in many countries as hormone disruptors.

Siloxanes are amazing substances and are used for their hydrophobicity, low thermal conductivity, and high flexibility.

Siloxanes (since 1940) are used in many cosmetic, electronic, household, fuel, automotive and medical device products. Exposure occurs from personal products, water, and food ingestion, wastewater, industrial processes, and sewage sludge.
Nanomaterials – the next miracle product

Very small particles engineered for special functions including catalytic behavior, high strength, thermal and electrical conductivity etc.

Biomedical, solar panels, water treatment etc

Emerging occupational hazard typically through inhalation

Regulation not keeping up
Microplastics

Microplastics are everywhere

In the air
In the soil
In the water
In our food

Even in your bottled water

Tiny shards of plastic less than 5,000 microns in length
EDC’s (Endocrine Disruptors)

EDC’s are chemicals that can interfere with the endocrine or hormone systems in the body.

Any system in the body can be affected.

Typical effects are tumors, birth defects, lower fertility, development disorders and immune systems.
Shortlist
<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Where</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permethrin</td>
<td>Pesticide formulations, bulk storage, spills</td>
</tr>
<tr>
<td></td>
<td>Neurotoxic to fish</td>
</tr>
<tr>
<td>1,4 Dioxane</td>
<td>Co-solvent, replaces chlorinated solvents</td>
</tr>
<tr>
<td></td>
<td>Food, cosmetics, children’s products</td>
</tr>
<tr>
<td></td>
<td>Landfills, very soluable in gw</td>
</tr>
<tr>
<td>PFOS, PFOA (perfluorinated)</td>
<td>Fire fighting foam, retardants</td>
</tr>
<tr>
<td></td>
<td>Adhesives, cosmetics, consumer products</td>
</tr>
<tr>
<td></td>
<td>Soluble in gw, sticky with soil, found in leachate</td>
</tr>
<tr>
<td></td>
<td>Endocrine disruptor</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Where</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Sulfolane and DIPA</td>
<td>Natural gas and LNG</td>
</tr>
<tr>
<td></td>
<td>Highly soluble in gw</td>
</tr>
<tr>
<td>MethylNaphthalene (alkylated PAH)</td>
<td>Oil and gas activities, drilling, production, processing, retail and storage</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Where</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>EE2 (estrogen, birth control)</td>
<td>Closure of Sewage Lagoons, Sewage Plant effluents. Fish population collapse in lakes and rivers at 0.005 ppb</td>
</tr>
<tr>
<td>Nonylphenol and ethoxylates (detergents and surfactants)</td>
<td>STP effluents, pesticides, pulp and paper, textiles, paint, fracking Endocrine disruptor</td>
</tr>
<tr>
<td>Triclosan and other antimicrobials</td>
<td>Skin exposure, thyroid impacts, plant toxicity, breakdown to dioxins</td>
</tr>
<tr>
<td>Chlorinated Alkanes (paraffins)</td>
<td>Lubricants, flame retardant, landfill, industrial sites</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Where</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Siloxanes</td>
<td>Personal products, food, wastewater, sewage sludge, car wax, fuel additive, landfill Endocrine disruptor</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>Landfill leachate, STP, sludge May effects on aquatic environment, drinking water</td>
</tr>
<tr>
<td>Microplastics</td>
<td>Face washes, toothpaste, laundry water Accumulate in organisms at all trophic levels – filter feeders, plankton and up Bind organic contaminants, transport toxins through ingestion</td>
</tr>
<tr>
<td>Contaminant</td>
<td>Where</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>Nanomaterials (nanosilver, nanocarbon)</td>
<td>3 dimensions &lt; 100 nm</td>
</tr>
<tr>
<td></td>
<td>Health and fitness products</td>
</tr>
<tr>
<td></td>
<td>Antimicrobial (socks, bandages, textiles)</td>
</tr>
<tr>
<td></td>
<td>Groundwater, STP, Leachate</td>
</tr>
<tr>
<td>PBDE’s (Polybrominated diphenyl ethers)</td>
<td>Landfill leachate, electrical and plastics manufacturing</td>
</tr>
</tbody>
</table>
Winners
Winners

Biggest short term impact on contaminated site work
PFAS

1,4-dioxane
### INTRODUCTION

#### PFOA and PFOS Structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Vapor Pressure</th>
<th>Aqueous Solubility</th>
<th>Log $K_{oc}$</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFOA</td>
<td>$C_{8}H_{15}F_{15}O_{2}$</td>
<td>0.1 kPa (20°C), 10 mm Hg (25°C)</td>
<td>4.1 g/L (22°C), 9.5 g/L (25°C)</td>
<td>2.06</td>
<td>Stable</td>
</tr>
<tr>
<td>PFOS</td>
<td>$C_{8}F_{17}SO_{3}^{-}$</td>
<td>$3.31 \times 10^4$ Pa at 20°C</td>
<td>570 mg/L</td>
<td>2.57</td>
<td>Stable</td>
</tr>
<tr>
<td>PFHxS</td>
<td>$C_{6}F_{13}SO_{3}$</td>
<td>0.61Pa (25°C)$^\text{ES}$</td>
<td>6.2 mg/L$^\text{ES}$, 22 mg/L</td>
<td>3.5$^\text{ES}$</td>
<td>Stable</td>
</tr>
<tr>
<td>PFBS</td>
<td>$C_{4}F_{9}SO_{3}$</td>
<td>0.29 mm Hg at 20°C</td>
<td>8900 mg/L$^\text{ES}$, 344 mg/L$^\text{ES}$</td>
<td>2.2$^\text{ES}$, 1.9$^\text{ES}$</td>
<td>Stable</td>
</tr>
<tr>
<td>6:2 FTS</td>
<td>$F(CF_{2})<em>{6}CH</em>{2}CH_{2}SO_{3}^{-}$</td>
<td>0.115Pa(25°C)$^\text{ES}$, 0.00086 mm Hg (25°C)$^\text{ES}$</td>
<td>11 mg/L$^\text{ES}$, 2mg/L$^\text{ES}$</td>
<td>4.0$^\text{ES}$</td>
<td>Biodegradable under specific conditions</td>
</tr>
</tbody>
</table>
Used to make clothes water and stain resistant. Means take a long time to break down in the environment

Easily glide through human blood

Catches and blocks growth and reproductive hormones

Nests in the human liver
# Health Canada PFAS Screening Values

<table>
<thead>
<tr>
<th>PFAS Name</th>
<th>Acronym</th>
<th>Drinking Water Screening Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(milligrams/litre) (mg/L)</td>
</tr>
<tr>
<td>perfluorooctanoic acid</td>
<td>PFOA</td>
<td>0.0002*</td>
</tr>
<tr>
<td>perfluorooctane sulfonate</td>
<td>PFOS</td>
<td>0.0006*</td>
</tr>
<tr>
<td>perfluorobutanoate</td>
<td>PFBA</td>
<td>0.03</td>
</tr>
<tr>
<td>perfluorobutane sulfonate</td>
<td>PFBS</td>
<td>0.015</td>
</tr>
<tr>
<td>perfluorohexanesulfonate</td>
<td>PFHxS</td>
<td>0.0006</td>
</tr>
<tr>
<td>perfluoropentanoate</td>
<td>PFPeA</td>
<td>0.0002</td>
</tr>
<tr>
<td>perfluorohexanoate</td>
<td>PFHxA</td>
<td>0.0002</td>
</tr>
<tr>
<td>perfluoroheptanoate</td>
<td>PFHpA</td>
<td>0.0002</td>
</tr>
<tr>
<td>perfluorononanoate</td>
<td>PFNA</td>
<td>0.000002**</td>
</tr>
</tbody>
</table>

* Full health risk assessments have been developed by Health Canada for PFOS and PFOA as part of the Guidelines for Canadian Drinking Water Quality. These two assessments underwent public consultation in 2016 and are expected to be published in 2018.

** Updated, July 2018.
States With Numerical PFAS Limits

Washington
- Banned in firefighting foam and food packaging
- Proposed drinking water standard

Vermont
- 20 PPT (PFAS)
- Drinking water health advisory for 5 PFAS

Massachusetts
- 70 PPT (PFAS)
- State guidance for concentrations of 5 PFAS in drinking water

New Jersey
- Set PFNA standard at 13 ppt
- Weighing proposed standards for: PFOA at 14 ppt
- PFOS at 13 ppt

California
- 14 PPT (PFOA)
- 13 PPT (PFOS)
- Drinking water notification guidance

Colorado
- PFOA/PFAS listed as hazardous waste
- 70 PPT (Combined PFOA/FFOS)
- Groundwater quality standard for El Paso County only

Minnesota
- 36 PPT (PFOA)
- 27 PPT (PFOS)
- Health-based guidance values

Michigan
- 70 PPT (Combined PFOA/FFOS)
- State standard for concentrations in drinking water
Treatment Objectives – 70 PPT (part per trillion)

70 ppt is equivalent to 70 drops of water diluted into 20, two-meter-deep Olympic-size swimming pools (50,000 m³)
Treatment Objectives – 70 PPT (part per trillion)

70 drops of ink dropped into Niagara falls over a 20 second period
Treatment Challenges - PFAS

Broad mixture
- Wide range of properties, long and short chain
- Hydrophobic and electrostatic effects

Low volatility

High Solubility
- long plumes

Treatment requirements to very low concentrations
Treatment Options

Excavation and Incineration
- expensive
- not suitable for on site treatment

Immobilization/Stabilization
- several approaches that can be successful to contain plumes
- powdered reagents and modified clay
- liquid carbon products
Treatment Options

Bioremediation
- aerobic not effective
- anaerobic has some effect but may produce toxic intermediates

Membrane Filtration (RO and Nanofiltration)
- generally rejects 99% of PFOS, but waste stream must be dealt with

Adsorption
- Activated carbon
Treatment Options

Ion Exchange
  - Resins
  - Zeolites
  - Biomaterials

Chemical Treatment
  - Chemical oxidation
  - Electrochemical
  - Plasma
Treatment Options - Focus

Carbon Adsorption

Typical pump and treat solutions

Ion Exchange

Some are treating potable well water
Treatment Options - GAC

• may have issues if lots of organics

• Pre treatment for iron, manganese or hardness may be required

• Disposal by incineration or reactivation (reduce long term liability)

• Performance varies with source material and activation method

• Can be an expensive option, but works
Treatment Options – Ion Exchange

- Resins exchange ions, can remove both long and short chain PFAS
- Typically contact time required is less than carbon, so smaller footprint
- Anionic resins successfully used
- Single use systems resin is used once then incinerated
- Regeneration systems can create hazardous waste stream, although techniques exist to regenerate with no waste products
Treatment Options – 1,4 Dioxane

No Federal guidelines in Canada or US

1,4 Dioxane miscible in water

Typical treatment will be ex-situ with advanced oxidation

Biological treatment may also be possible

<table>
<thead>
<tr>
<th>State</th>
<th>Guideline (µg/L)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alaska</td>
<td>77</td>
<td>AL DEC 2015</td>
</tr>
<tr>
<td>California</td>
<td>1.0</td>
<td>Cal/EPA 2011</td>
</tr>
<tr>
<td>Colorado</td>
<td>0.35</td>
<td>CDPHE 2017</td>
</tr>
<tr>
<td>Connecticut</td>
<td>3.0</td>
<td>CTDPH 2013</td>
</tr>
<tr>
<td>Delaware</td>
<td>6.0</td>
<td>DE DNR 1999</td>
</tr>
<tr>
<td>Florida</td>
<td>3.2</td>
<td>FDEP 2005</td>
</tr>
<tr>
<td>Indiana</td>
<td>7.8</td>
<td>IDEM 2015</td>
</tr>
<tr>
<td>Maine</td>
<td>4.0</td>
<td>MEDEP 2015</td>
</tr>
<tr>
<td>Massachusetts</td>
<td>0.3</td>
<td>MADEP 2004</td>
</tr>
<tr>
<td>Mississippi</td>
<td>6.09</td>
<td>MS DEQ 2002</td>
</tr>
<tr>
<td>New Hampshire</td>
<td>0.25</td>
<td>NH DES 2011</td>
</tr>
<tr>
<td>New Jersey</td>
<td>0.4</td>
<td>NJDEP 2015</td>
</tr>
<tr>
<td>North Carolina</td>
<td>3.0</td>
<td>NCDENR 2015</td>
</tr>
<tr>
<td>Pennsylvania</td>
<td>6.4</td>
<td>PADEP 2011</td>
</tr>
<tr>
<td>Texas</td>
<td>9.1</td>
<td>TCEQ 2016</td>
</tr>
<tr>
<td>Vermont</td>
<td>3.0</td>
<td>VTDEP 2016</td>
</tr>
<tr>
<td>Washington</td>
<td>0.438</td>
<td>WA ECY 2015</td>
</tr>
<tr>
<td>West Virginia</td>
<td>6.1</td>
<td>WV DEP 2009</td>
</tr>
</tbody>
</table>
THANK YOU