

Emerging Contaminants – a Primer

Bob Kennedy 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 aquafer



Cosmetics

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



Applications of Engineered Nanoparticles (ENPs)



- ~1,300 items in consumer products (2011)
- 520% increased from 2006
- Potential for broad range of future applications (www.nanotechproject.or g)
- ➔ Growing concerns over adverse effects of ENPs to biota

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



Contaminant	Where
Permethrin	Pesticide formulations, bulk storage, spills Neurotoxic to fish
1,4 Dioxane	Co-solvent, replaces chlorinated solvents Food, cosmetics, children's products Landfills, very soluable in gw
PFOS, PFOA (perfluorinated)	Fire fighting foam, retardants Adhesives, cosmetics, consumer products Soluble in gw, sticky with soil, found in leachate Endocrine disruptor



Contaminant	Where
Sulfolane and DIPA	Natural gas and LNG Highly soluble in gw
Methylnaphthalene (alkylated PAH)	Oil and gas activities, drilling, production, processing, retail and storage



Contaminant	Where
EE2 (estrogen, birth control)	Closure of Sewage Lagoons, Sewage Plant effluents. Fish population collapse in lakes and rivers at 0.005 ppb
Nonylphenol and ethoxylates (detergents and surfactants)	STP effluents, pesticides, pulp and paper, textiles, paint, fracking Endocrine distruptor
Triclosan and other antimicrobials	Skin exposure, thyroid impacts, plant toxicity, breakdown to dioxins
Chlorinated Alkanes (paraffins)	Lubricants, flame retardant, landfill, industrial sites



Contaminant	Where
Siloxanes	Personal products, food, wastewater, sewage sludge, car wax, fuel additive, landfill Endocrine disruptor
Pharmaceuticals	Landfill leachate, STP, sludge May effects on aquatic environment, drinking water
Microplastics	Face washes, toothpaste, laundry water Accumulate in organisms at all trophic levels – filter feeders, plankton and up Bind organic contaminants, transport toxins through ingestion

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Contaminant	Where
Nanomaterials (nanosilver, nanocarbon)	3 dimensions < 100 nm Health and fitness products Antimicrobial (socks, bandages, textiles) Groundwater, STP, Leachate
PBDE's (Polybrominated diphenyl ethers)	Landfill leachate, electrical and plastics manufacturing



Winners





Winners

Biggest short term impact on contaminated site work







1,4-dioxane



INTRODUCTION





	Formula	Vapor Pressure	Aqueous Solubility	Log K _{oc}	Degradation
PFOA	C ₈ HF ₁₅ O ₂	0.1 kPa (20°C) 10 mm Hg (25°C)	4.1 g/L (22°C) 9.5 g/L (25°C)	2.06	Stable
PFOS	C ₈ F ₁₇ SO ₃ -	$3.31x10^4\text{Pa}$ at 20°C	570 mg/L	2.57	Stable
PFHxS	$C_6F_{13}SO_3$	0.61Pa (25°C) ^{ES}	6.2 mg/L ^{ES} 22 mg/L ^{ES}	3.5 ^{ES}	Stable
PFBS	$C_4F_9SO_3$	0.29 mm Hg at 20°C	8900 mg/L ^{ES} 344mg/L ^{ES}	2.2 ^{ES} 1.9 ^{ES}	Stable
6:2 FTS	F(CF ₂) ₆ CH ₂ CH ₂ SO ₃ ⁻	0.115Pa(25°C) ^{ES} 0.00086 mm Hg (25°C) ^{ES}	11 mg/L ^{ES} 2mg/L ^{ES}	4.0 ^{ES}	Biodegradable under specific conditions





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

DEAC Morro	A	Drinking Water Screening Value		
FFAS Name	Астопуш	(milligrams/litre) (mg/L)	(micrograms/litre) (µg/L)	
perfluorooctanoic acid	PFOA	0.0002*	0.2*	
perfluorooctane sulfonate	PFOS	0.0006*	0.6*	
perfluorobutanoate	PFBA	0.03	30	
perfluorobutane sulfonate	PFBS	0.015	15	
perfluorohexanesulfonate	PFHxS	0.0006	0.6	
perfluoropentanoate	PFPeA	0.0002	0.2	
perfluorohexanoate	PFHxA	0.0002	0.2	
perfluoroheptanoate	PFHpA	0.0002	0.2	
perfluorononanoate	PFNA	0.00002**	0.02**	

* 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





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

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

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





THANK YOU

