Emerging Contaminants Update with an Emphasis on 1,4-dioxane and PFASs found in Fire Fighting Foam

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Emerging Contaminants

Hazardous materials or mixtures that are characterized as having:

- A "perceived" or real threat to health, public safety, or the environment
- No published health standards or guidelines
- Limited toxicological information or under re-evaluation
- A significant new source, pathway, or detection limits
- "New" ECs (recently manufactured or introduced into commerce)
- "Old" ECs (legacy chemicals with newly identified/understood issues)



Early Identification/Risk – US Programs

- EPA Computational Toxicology Projects
 - Tox21 Toxicology Testing in the 21st Century; ToxCast Toxicity Forecaster;
 V-Embryo Virtual Embryo
- Other EPA Programs
 - Integrated Risk Information System (IRIS) database
 - EPA Office of Superfund Remediation and Technology Innovation (OSRTI) Provisional Peer-Reviewed Toxicity Values (PPRTVs)
 - Toxic Substances Control Act (TSCA) Work Plan for Chemical Assessments
- US Department of Health and Human Services
 - National Toxicology Program (NTP)
 - Agency for Toxic Substances & Disease Registry (ATSDR)







Well Emerged Example: 1,4-Dioxane



1,4-Dioxane Introduction

- What caused "emergence"? Lab detection limits, health impacts, inhalation risk
- Primarily used as a 1,1,1-trichloroethane stabilizer (>95% of 1970's production)
- Toxicology
 - Hepatotoxic, neurotoxic
 - "Likely to be carcinogenic in humans"
- Potentially low remediation goals
 - June 2015 US EPA issued a 0.46 ug/L Regional
 Screening Level for tap water
- Why not an issue in Canada/Europe/Australia? Not a POP!



1,4-Dioxane Occurrence

UCMR3 Results as of January 2016

4,035 Detections out of 34,684 Analyses = 12% Detection Rate



1,4-Dioxane vs Plume Length



n – 103 sites where 1,4-dioxane and chlorinated solvents occur

(Adamson et al, 2014)

International Regulations/Guidance

Country/NGO	GW (μg/L)	Notes			
Germany	0.1	Precautionary Guideline Limit			
US Environmental Protection Agency	0.35/0.46	Health advisory level/RSL			
France	6.6/37.5	Potable water limit/Risk threshold			
Japan	50	Adopted WHO threshold			
WHO (World Health Organization)	50	Suggested threshold			
Australia	77	Groundwater cleanup level			

Remediation Challenges

- Miscible in water (infinite solubility)
- Migrates rapidly, sorbs minimally
- Biologically recalcitrant
- Commonly co-mingled with CVOCs and metals
- Potentially low remediation goals
- Chemical properties result in large dilute plumes (<20 μg/L) with few "source areas" to address
- Existing CVOC remedies (e.g., air stripping, air sparge, GAC, ERD, KMnO₄) are relatively ineffective



Soil Remediation Technologies

- Not commonly found in soil
- Volatile if water is absent
- SVE/DPE can be effective once vadose zone is dewatered
- Thermal treatment/SVE
- Steam stripping/SVE
- XSVE Hinchee, et al ESTCP
- Off-gas could be direct vented (atmospheric half-life is 7 days), or treated with vapor-phase GAC or thermally oxidized
- Dig & haul to landfill or incinerate



Ex Situ

- Granular activated carbon ineffective
- DOW AMBERSORB 563[™] resin
 - Better than 99% removal rates
 - Applied to up to 45,000 $\mu g/L$ DX
 - Complex system engineering
- Advanced Oxidation Technologies (AOT)
 - Ozone + Peroxide
 - Ozone + ultraviolet light





In Situ Technologies







Oxidation

- Sodium persulfate
- Catalyzed hydrogen peroxide/ Fenton's chemistry
- Slow release permanganate
- Biodegradation
 - Metabolic or co-metabolic
 - Dominantly lab tested
 - Propane biostimulation field pilot tested
 - May only require oxygen addition
 - Thermal
 - Field demonstrated
 - Temps approach boiling point of water and DX is released, captured in vapour stream

ISCO – Project Example



MNA: Project Example

- International Fortune 100 company, CH2M supporting another consultant
- Assessed MNA solution for long-term management
- Landfill w/ long monitoring history, 15 yrs of 1,4-DX data
- Empirical data (calibrated model, mass balance): indicated attenuation is occurring, mechanism undefined
- Concentrations declined, dramatically since depletion of THF
- CSIA performed, but showed minimal enrichment
- Recommended UCLA test for 1,4-dioxane biomarkers
 - Dioxane monooxygenase (DXMO)
 - Aldehyde dehydrogenase (ALDH)
- Useful results, as weight of evidence for MNA

DXMO/ALDH Results



Phytoremediation

- Phytotranspiration process documented in research and field applications
- Accepted remedy at North Carolina industrial site
- Can be used for dewatering or containment (good for miscible 1,4-dioxane)
- Successfully applied as engineered wetlands
- Project in Netherlands showed healthy tolerance of 822,000 ug/L DX and dramatic reductions



Rapidly Emerging Example: Per- and Polyfluoroalkyl Substances (PFASs)



Per- and Polyfluoroalkyl Substances Introduction

- Heat, oil, stain, and grease resistant coatings
 - Clothing
 - Furniture
 - Food packaging
 - Non-stick cooking surfaces
 - Electrical wire insulation
- Fluorosurfactants
 - Aqueous film-forming foam (AFFF)
 - Electrochemical vs fluorotelomer based
 - Chromium plating mist suppressants
 - Photolithographic chemicals
 - Many other uses









US Drinking Water Analytical Results (January 2016)

273 Detections out of 35,060 Analyses = 0.8% Detection Rate



(USEPA, March 2016)

USAF – 10 Base Site Investigation Program

10 bases chosen for snapshot 4 locations selected per base

Location Category	% PFOS Detects	% PFOS Exceeds	% PFOA Detects	% PFOA Exceeds
Hangars and Buildings	84.8	70.9	89.9	45.6
Testing and Maintenance	86.4	77.3	77.3	54.5
Emergency Response	70	45	85	55
Waste Management	94.7	68.4	84.2	26.3

(After Long, 2015)

- FTAs excluded; looked at spray test areas, hangar releases, stormwater outfalls, aircraft/drone/missile crashes, AFFF storage/tanks/ponds, etc.
- Samples compared to US EPA Residential Screening Levels for solids or Provisional Health Advisory Levels for groundwater and surface water
- 16 PFASs analyzed, but results focused on PFOS and PFOA
- Detections and exceedances were greatest in groundwater

Representative International Drinking Water Screening Levels

Country / Type (year) (µg/L)	PFOA	PFOS	Other PFAS
Canada / drinking water screening value (2016)	0.2	0.6	PFBA, PFBS, PFHxS, PFPeA, PFHxA, PFHpA, PFNA
Denmark / health-based criteria (2015); if all 3 present, sum of ratios of conc:SL should be <1.	0.3	0.1	0.1 (PFOSA)
Germany / precautionary value, long-term (2006)	0.1 (PFOA	A + PFOS)	
Netherlands / provisional DW standard (2010)		0.53	
Sweden / maximal tolerable level (2014)	0.09 (sum of 7 PFAS)		PFHxS, PFBS, PFHpA, PFHxA, PFPeA
UK / DW quality guideline (2009)	10	0.3	

Remediation Technologies

• Soil

- Dig and haul to landfill, dig and incinerate
- Capping/encapsulation
- In situ stabilization/solidification (RemBind, MatCare, carbon, biochar, etc.)
- Groundwater
 - Ex situ
 - Proven (with limitations): GAC, anion exchange resins, reverse osmosis
 - Unproven: oxidation, bioreactors
 - In Situ
 - Proven (with limitations): sorption
 - Unproven: Oxidation, bio (fungal)

What's Next???



Who knows!!

- Fuel oxygenates (EDB, TBE)
- Hexavalent Chromium
- Phenols
- Phthalates
- PAH Mixtures
- Nanomaterials
- Pharmaceuticals and Personal Care Products (PPCPs)
- Sulfolane
- ????????

		Duplicate alert									
		Shade for data quality alert - more data needed	d?								
DOD 💌	Weighte - Rank		•	DOD EC	atch/Actio	on List Not	Captured	by this Screening			UPDATED (Jan 17 2014)
Watch	1	1.4-Dioxane		Watch Li	st					1	1.4-Dioxane
Watch	2	Nickel, Ni		Decabro	modiphenv	Ether (De	ca-BDE)			2	Nickel, Ni
watch	3	his(2-ethylbeyyl) nhthalate (BEHP/DEHP)		Diisocyar	nates					3	his(2-ethylbexyl) nbthalate (BEHP/DEHP)
Watch	4	Cadmium, Cd		Dioxins	lates					4	Cadmium, Cd
	5	1.3-Butadiene		Tetrachlo	proethylene	PCF)				5	1.3-Butadiene
	6	2.4-Diaminotoluene								6	2.4-Diaminotoluene
	6	2.4-Toluenediamine		Phase II	Action List					6	2.4-Toluenediamine
Phase II	6	Nanhthalene		Berylliun	n					6	Nanhthalene
	9	N-Nitrosodiethyamine (NDEA)		Sulfur He	exafluoride	(SF6)				9	N-Nitrosodiethvamine (NDEA)
	10	Ethylene Dibromide		Trichloro	ethylene (1	TCE)				10	Ethylene Dibromide
	10	Nitrobenzene		1-Bromo	propane (1-	BP)				10	Nitrobenzene
Dropped	12	1.2.3-Trichloropropage (1.2.3-TCP)								12	1.2.3-Trichloropropane (1.2.3-TCP)
Phase II	12	Lead. Pb		Future A	ssessments					12	Lead. Pb
	14	Pentachlorophenol		2.4-Dinit	roanisole ([DNAN)				14	Pentachlorophenol
Dropped	15	1.4-Dichlorobenzene		5-Nitro-1	.2.4-triazol	-3-one (NT	ro)			15	1.4-Dichlorobenzene
	16	o-Toluidine								16	o-Toluidine
	17	Benzidine								17	Benzidine
	18	2.4.6-Trichlorophenol								18	2 4 6-Trichlorophenol
	19	Aniline								19	Aniline
	20	Methyl Oxirane (Propylene oxide)								20	Methyl Oxirane (Pronylene oxide)
	20	4-Chloroaniline								21	Chromium bexavalent Cr(VI)
Future	21	N-nitroso-dimethylamine (NDMA)								22	4-Chloroaniline
Future	23	Metolachlor								22	N-nitroso-dimethylamine (NDMA)
	24	Arsenic As	no rev							24	Metolachlor
	25	Hexachlorobenzene	noret							25	Arsenic As
	26	Chromium (r (total)	This seen	ns overstat	ed in comn	arison to P	Hey Chrom	0		26	Hevachlorobenzene
iim hartlev:	20	Chromium beyavalent Cr(VI)	In Feb 2012	504 doublook	ad a namechod		ating the IRIS	-	cmont which can be found in I	Lo Track (IP 27	Benz[a]anthracene
Much reduce	d	Benzfalanthracene								28	Cobalt. Co
		Cobalt. Co								28	N-Nitrosodi-n-propylamine (NDPA)
		N-Nitrosodi-n-propylamine (NDPA)								30	2 4-Dinitrotoluene
Watch	31	2.4-Dinitrotoluene								30	Molybednum, Mo
Water	31	Molybednum Mo								32	4 4'-Diaminodinbenylmethane
	33	4.4'-Diaminodiphenylmethane								33	4.4'-Oxydianiline
	34	4 4'-Oxydianiline								34	Mercury Hg
	35	Mercury Hg								35	1 2-Dichlorobenzene
Dronned	36	1 2-Dichlorobenzene								36	4 4'- Methylenebis (2-chloroaniline)
bropped	37	4 4'-Methylenebis (2-chloroaniline)								36	Renzo[2]nvrene
	37	Benzo[2]pyrene								36	Benzo[b]fluoranthene
	37	Benzo[b]fluoranthene								36	Dibenz(a blanthracene
	27	Dihonala hlanthracana								26	Dimetheste
	27	Dimethoato								41	HovePP
Dronned	/2	HevaBB		-						41	Ethylene oxide
Dropped	42	Ethylopo oxido								42	2.4 Dichlorophonol
	45	2.4 Dishlaranhanal								43	2,4-Dichlorophenol
	44	2,4-Dichlorophenol								444	1 1 Disklaraathana
	45	1 1 Dishlarasthana								45	1,1-Dichloroethalle
Rhaco II	40	1,1-Dicilioroetilane	Phthalat	a actors ray	ommondoo	for Phace	II / Action	List		45	biethyi phthalate
r nase ll	40	Budratino	Finnulut	c csters fet	.ommendeu	i joi riidse	/ ACLION	LIST		45	N pitrocopyrroliding (NBVP)
	40	N pitrocopyrroliding (NDVP)								45	Vanadium V
Mat-l-	40	Venedium V		-	-		-			49	
watch	50	vanaurum, v			-					50	1, 2, 4, 5- retrachiorobenzene
	51	1,2,4,5-Tetrachlorobenzene								50	2-Naphtylamine
	51	2-Naphtylamine								50	3,3-Dimethylbenzidine
	51	3,3-Dimethylbenzidine								50	4-Aminobiphenyl
	51	4-Aminobiphenyl								50	Benzyl chloride
	51	Antimicrobial Agents								50	dimethyl phthalate
	51	Antocorrosive agents								50	Indenol 1.2.3-cd pyrene

Thank you for your time

Questions?

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