EMERGING CONTAMINANTS – CHALLENGES FOR CONSULTANTS AND LABORATORIES

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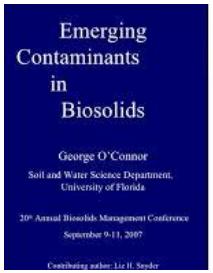
Content

- What do we mean by Emerging Contaminants
- Characteristics and Challenges posed by topical EC
- Closing Thoughts



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Emerging Contaminants?

- Google “Emerging Contaminants” approx. 2,000,000 hits
- ‘EC’ not new but growing focus / trend over last 10 years
- Dedicated EC Organisations:
  - NORMAN (2009)
  - CREEC (2010)
  - NICOLE Working Group (2014)
- Dedicated EC International Conferences:
  - EmCon 2016 (5th Conference since 2007)
  - Emerging Contaminants Summit 2016
- Numerous Definitions for EC

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CREEC - The Consortium for Research and Education on Emerging Contaminants
NICOLE – Network for Industrially Contaminated Land in Europe
NORMAN - Network of reference laboratories, research centres and related organisations for monitoring of emerging environmental substances

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Emerging Contaminants?

Chemicals & materials that have pathways to enter the environment and present potential unacceptable human health or environmental risks…and either do not have peer-reviewed human health standards Or Standards/ regulations are evolving due to new science, detection capabilities, or pathways.
(US Department of Defence)

Previously undetected organic micro pollutants are being observed in the aqueous environment due to improvements in analytical techniques. These are known as emerging contaminants. Many of these are currently unregulated. Some of these contaminants can have human or ecological health effects and there is a need for better understanding.
(UK BGS)

"Emerging environmental substances are not necessarily new chemicals. They are substances that have often long been present in the environment but whose presence and significance are only now being elucidated".
(NORMAN)

An emerging contaminant (EC) is a chemical or material characterized by a perceived, potential, or real threat to human health or the environment or by a lack of published health standards. A contaminant also may be "emerging" because of the discovery of a new source or a new pathway to humans.
(US EPA)

Emerging contaminants (ECs) are those chemicals that recently have been shown to occur widely in water resources and identified as being a potential environmental or public health risk, and yet adequate data does not exist to determine their risk.
(Drewes and Shore 2001, Younos, 2005).

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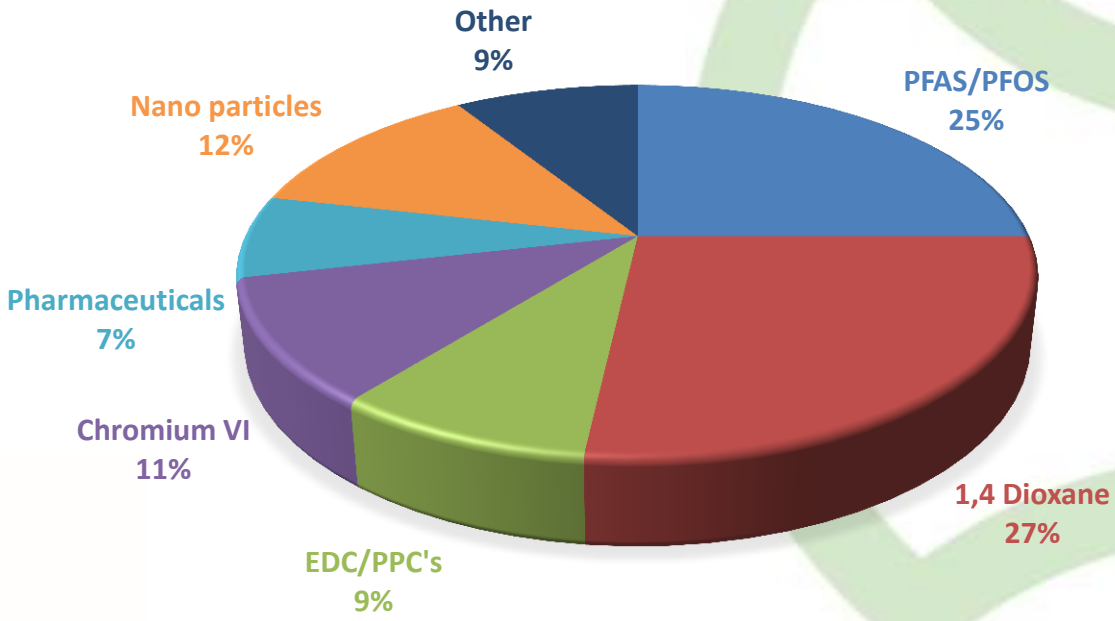
Emerging Contaminants?

- 14 million commercially available substances in US < 2% regulated *(Florida DOEP 2008)*. Likely many more now!
- NORMAN nearly 1,000 substances on Watch List;
- US DOD has 33 substances on Watch/Action Lists;
  - includes 'common contaminants'; Nickel, Cadmium, Lead, TCE & Naphthalene?
- Actual substances considered as Emerging depends on the problem holder
- Often more apt "Contaminants of Emerging Concern". Its the concern that's emerging not the contaminant.

Global Emerging Contaminants

- Some consensus type of EC of Global Concern Include;
  - surfactants, flame retardants, pharmaceuticals and personal care products, gasoline additives and their degradation products, biocides, polar pesticides and their degradation products, nano particles, and various proven or suspected endocrine disrupting compounds.
- Emerging Contaminants Summit 2016: Platform Presentations



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EC Common Attributes

- Termed EC on the basis of a selection of the following;
  1. Potential to represent unacceptable risks to human health or environment
  2. Previously unregulated or no standards or standards evolving
  3. Not necessarily new substance but only recently detected or found to be so widespread in the environment
  4. Inadequate information to properly determine significance of risk.
- But the risks presented and challenges posed can be completely different from one EC substance to the next!
- PFOS & 1,4-Dioxane Examples

PFOS: Characteristics

- 'Perfluorooctane Sulfonic Acid' but not a single substance: $C_8F_{17}SO_2X$ (X=OH, metal salt, other)
- OECD 2002 - 48 to 172 PFOS substances (inc. PreFOS)
- Widespread Global use since 1950's
  - **Soil, Water, Oil resistance for Fabric & leather**; GPV2000 c. 2,160 tons
  - **Grease, Oil, Water resistance to paper and board;** GPV2000 c. 1,490 tons
  - **Performance chemicals**; GPV2000 c. 831 tons, inc.151 tons fire foams.
- Direct emissions 1970-2002: estimate PreFOS c.50,000 tons

PFOS: Characteristics

- Current use is highly restricted but NOT banned
- Restrictions on new products only (after 2008)
- COT & HPA Proposed DWS of 0.3ug/l
- Directive 2013/39/EU set a sub ppt EQS for PFOS,
  - PFOS = Perfluorooctane sulfonic acid and its derivatives
  - Implement EQS by 2018 (take into account in monitoring programmes)
  - Achieve good surface water chemical status by 2027

Surface Water EQS				Biota
AA FW	AA M	MAC FW	MAC M	(Fish)
µg/l	µg/l	µg/l	µg/l	µg/kg (W/W)
0.00065	0.00013	36	7.2	9.1

PFOS: Characteristics

- Behaviour in the Environment

	Benzo(a)pyrene	PFOS	Benzene	
Water Solubility (mg/l)	0.0038	519	1,780	Quite Water Soluble
Air Water Partition Coefficient	1.76E-06	<2xE-06	1.16E-01	Low Volatility
Log Koc (cm^3/g)	5.11	2.57	1.83	Intermediate potential to bind to Soil Organic Matter
Bioconcentration Factor (L/kg)	2657	2800	30	Very High Potential to Bioaccumulate (binds to proteins in blood and liver rather than fatty tissues)
Biomagnifcation Factor	2	5	1	Very High Potential to magnify through the food chain (value adopted for EQS)
Half life in water (yrs.)	0.3 - 2.9	>41	0.08 – 0.5	Very Very Persistent

  - If used for 60 years has any degraded?

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PFOS: Use Challenges

- Widespread use in everyday products such as coatings to fabrics and personal care products such as shampoos & cosmetics;
  - High likelihood that equipement manufactering, field staff and analysts could be sources of PFOS
  - Not practical to restrict use so must adopt appropriate coverals, nitrile gloves etc.
- Previously thought 'Inert' equipement sources of PFC such as teflon;
  - Use teflon free tubing and caps, containers.
- Include analysis of trip, equipement and lab blanks within sampling programme.

Cross Contamination During Sampling and Analysis
Very High Possibility

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PFOS: Occurrence Challenges

- Primary Sources
  - Flourochemical industry
  - Metal Plating / Etching
  - Manufacturing – Textiles, PCP, Cleaners
  - Fire Fighting Foams – how were stocks reduced 2011?
  - Hydraulic Fluids in Aviation
  - And more…….
- Secondary Sources
  - Waste Management – Recycling/Landfilling
  - Waste Water Treatment Works inc bio-solids
- Low volatility, soluble, moderate Koc, persistent = Potential to undergo long range transport - found in the Arctic!
- Environment Canada - “Ubiquitous in the Environment”

PFOS: Occurrence Challenges

- EU Wide Survey 2007 (*RIVM 2010*)
  - 122 sampling locations streams & rivers in 27 countries
  - PFOS detected in 97% of samples (>1ng/l) i.e. above the AA EQS

Summary Recorded PFOS Concentrations (ng/l)					
Min	Median	Mean	90th%	Max	AA EQS
<1	6	39	73	1371	0.65

  - Noted 'high' concentrations not close to obvious Point Source;
    - River Seine France – 97ng/l
    - River Severn UK – 238ng/l
    - River Rhine Germany – 32ng/l
- Robust CSM, identify other sources and measure 'background'

Likelihood EQS Exceeded from Diffuse Sources
Very High

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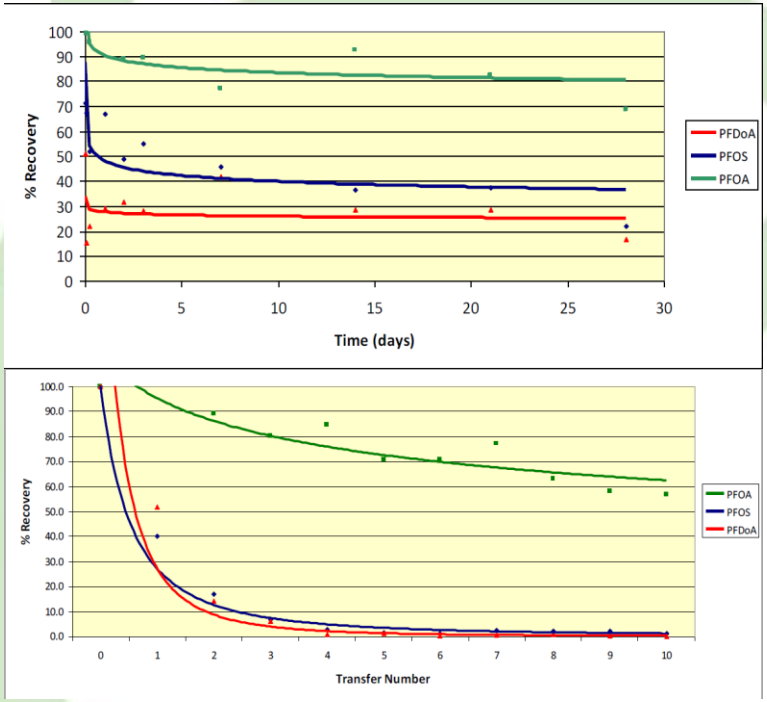
PFOS: Analytical Challenges

- EQS Related!
  - PFOS EQS (0.65ng/l) “Perfluorooctane sulfonic acid and its derivatives” its not a single substance.
  - Not fully understood what derivatives detected and measured.
  - ISO 25101 Method LC/MS for concentrations ranging from 2ng/l to 10,000ng/l depending on the matrix
  - Commercial labs offering LOD around 10-50ng/l ‘clean water’
  - Environmental samples more problematic due to matrix interferences raising LOD or requiring clean up

LOD Very Likely to be Greater than EQS and Possibly DWS

PFOS: Analytical Challenges

- Proficiency testing schemes - poor data reproducibility
  - Background Contamination - Analyst & PFC containing equipment.
  - Poor Recovery
- Glassware adsorption
  - >50% loss in recovery after 2-3 days but depends on SA/V Ratio
  - Use polypropylene/polyethylene containers for all standard, sample and extraction preparations.
- Multiple Transfers
  - > 50% loss in recovery per transfer



Maxxam 2012

Poor Analytical Data Reproducibility

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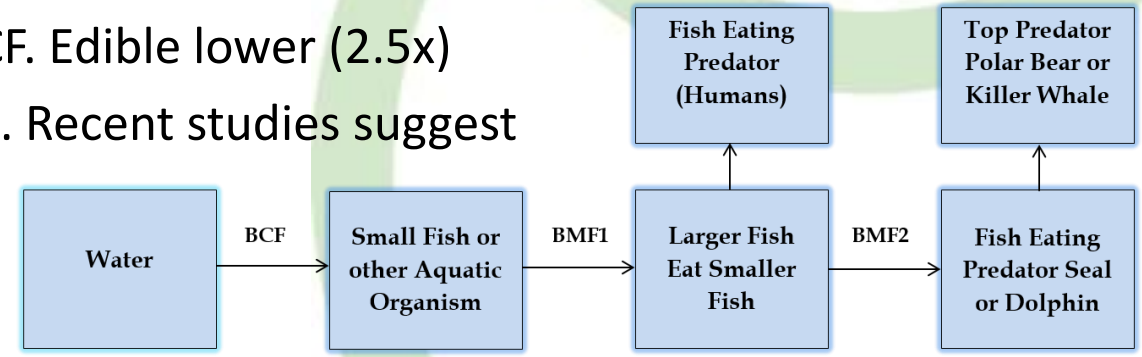
PFOS: Assessment Challenges

- Why is the AA EQS so low anyway?
- Very Conservative Assumptions, 200-500 x lower!
- Secondary Poisoning
  - Allocation of TDI to Fish Default 10% - Recent Studies Show 75% (7.5x)
  - Technical Guidance Note 27 misquotes the consumption rate of 0.115kg/day as the 'European Average'? (4x)
  - Adopts whole Fish BCF. Edible lower (2.5x)
  - BMF of 5. Default is 2. Recent studies suggest 2 high (2.5x-6.25x)
- Useful benchmark?



EQS Probably Already Outdated by Newer Studies

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1,4 Dioxane: Characteristics

- Cyclic ether $C_4H_8O_2$ flammable liquid with faint pleasant odour
- 90% as solvent stabiliser especially TCA (2-5% v/v) but also
  - 1,4-D is a good solvent in its own right
  - paints, resins, cellulose acetate, paint/varnish strippers, PET plastic bottles, automotive coolants, fumigants, dyes, pharmaceuticals, pesticides, adhesives and magnetic tape.
- By-product of ethoxylation of ethylene oxide used in shampoos, lotions, liquid soaps etc.
- GPV c.14,000 tonnes in 1985 but big decrease due to phasing out of TCA use (1005/2000/EC)

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1,4 Dioxane: Characteristics

- Limited Specific EU/UK Regulation
  - Prohibited from Cosmetic Products Reg. 1223/2009/EC
  - CLP Regs: flammable, eye/respiratory irritant, Suspected Carcinogen
- No EU/UK specific DWS
  - WHO DWS 50ug/l (2005)
  - US States lower 0.3ug/l (Massachusetts) – 3 ug/l (Connecticut)
- No Statutory EQS
  - PNEC Surface Water 57,500ug/l (EU RAR 2002)

1,4 Dioxane: Characteristics

- Behaviour in the Environment

	Benzo(a)pyrene	1,4 D	Benzene	
Water Solubility (mg/l)	0.0038	1,000,000	1,780	Very Water Soluble
Air Water Partition Coefficient	1.76E-06	2.1E-04	1.16E-01	Moderately Volatile
Log Koc (cm^3/g)	5.11	0.09	1.83	Very Low potential to bind to Soil Organic Matter
Bioconcentration Factor (L/kg)	2657	<1	30	Very Low Potential
Biomagnifcation Factor	2	Low	1	Low Potential
Half life in water (yrs.)	0.3 - 2.9	>1	0.08 – 0.5	Relatively Persistent

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1,4 Dioxane: Use Challenges

- Although banned in cosmetics in EU, may be by product and not so elsewhere such as U.S.;
  - Potential for equipement manufactering, field staff and analysts could be sources of 1,4 D
  - Not practical to restrict use so must adopt appropriate coverals, nitrile gloves etc.
- PET used in manufacture of plastic bottles & Polyester fabrics;
  - Use Glass avoid PET Plastic bottles
  - Precaution also avoid polyester
- Include analysis of trip, equipement and lab blanks within sampling programme.

Cross Contamination During Sampling and Analysis Significant Possibility

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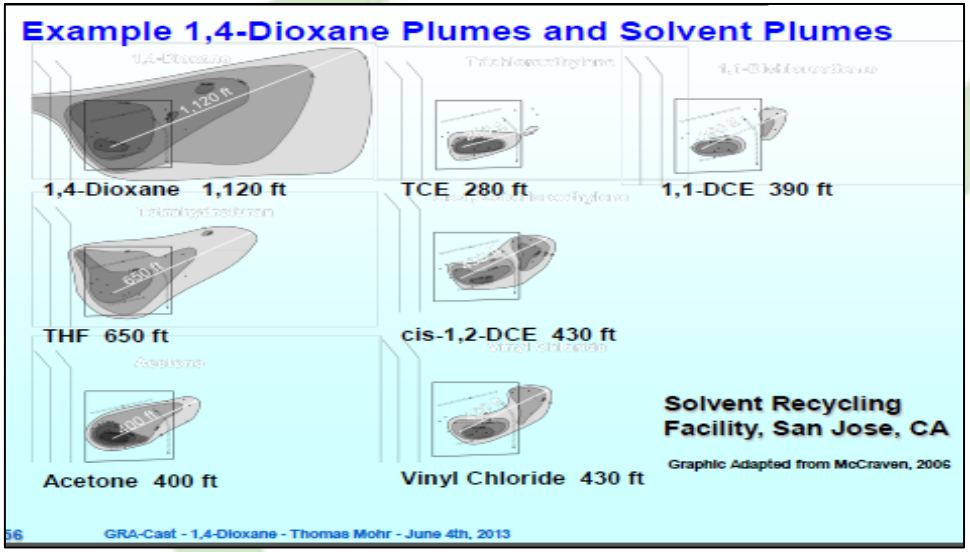
1,4 Dioxane: Occurrence Challenges

- High solubility and low soil adsorption, little retardation - migration well ahead of co-released CVOCs
- Not amenable to many traditional CVOC treatments inc. Anearobic Bio or ZVI
- May still be present where previously 'treated' solvent plumes.
- Oxidation currently most effective but size of plumes means very expensive.



Doesn't attenuate quickly and plume keeps growing!

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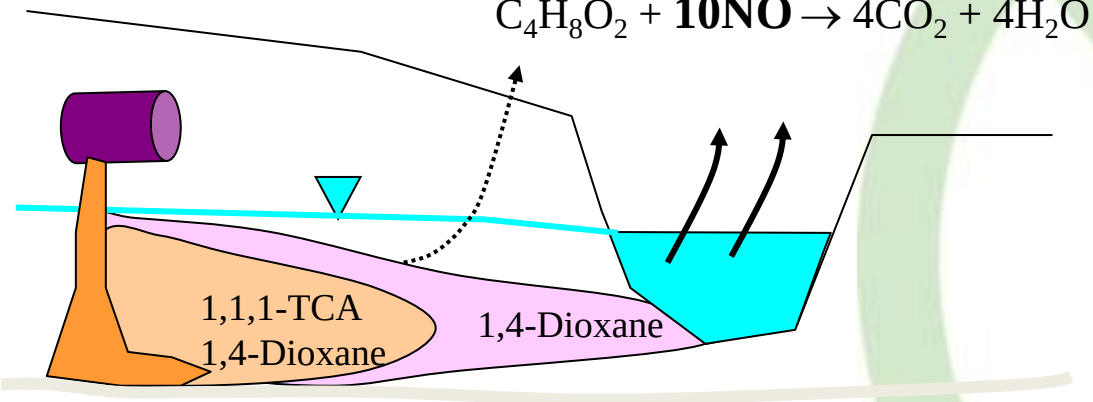
1,4 Dioxane: Occurrence Challenges

- Biological stable and does not hydrolyze
- Untreated Primary fate atmospheric oxidation – but slow transfer
- Potential VI issue but short half life in atmosphere (<1day)

$$C_4H_8O_2 + \mathbf{10NO} \xrightarrow{UV} 4CO_2 + 4H_2O + 5N_2$$



Vapour Intrusion Above Long Plumes Needs Consideration

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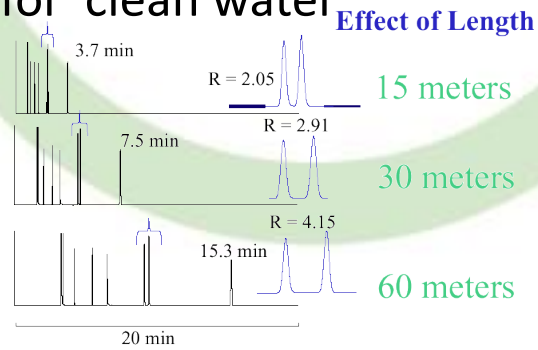
1,4 Dioxane: Analytical Challenges

- Detection previously limited by analytical methods “unseen.”
  - Historically, analysed as VOC High LOD –100 to 250 µg/L due to very high solubility - inexpensive
  - Later analysed as SVOC LLE lowered LOD - 5-10 µg/L
  - Introduction of SPE, lowering LOD to 0.05 µg/L for ‘clean water’
  - But doesn't use a standard SVOC GC column. While still non routine expensive and minimum sample volumes often required to be viable.



- Low mass ions potential for interferences
- Cross Contamination Issues not fully understood.
  - High laboratory background levels with SVOC method thought likely to be associated with air contamination.

Analysis to Low Levels Relatively Expensive While Still Non-Routine

Closing Thoughts

- Challenges Differ?

	PFOS	1,4 Dioxane
Use Profile	Very Varied	Varied
Regulation	Highly Regulated	Little Regulation
Quality Standards	Very Low	Moderate
Persistence	Very Persistent	Persistent
Mobility	Moderate	Very Mobile
Occurrence in Environment	Ubiquitous	Localised but distant from source
Cross Contamination	Very High Potential	Potential
Low LOD	Not achievable	Costly to achieve
Available information	Much available but still unknowns	Much available but still unknowns

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Closing Thoughts

- PFOS & 1,4 Dioxane Why Emerging?
  - Neither new but now being found at more sites largely due to lowering of analytical detection limits
  - Introduction of new regulations and or lowering of standards causing problems at more sites
  - Persistent and or mobile with potential to migrate significant distances
  - Represent unacceptable risks to human health or environment
  - Inadequate information to properly determine significance?

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